

# Neutron vibrational spectroscopy and first-principles calculations of the ternary hydrides $\text{Li}_4\text{Si}_2\text{H}(\text{D})$ and $\text{Li}_4\text{Ge}_2\text{H}(\text{D})$ : Electronic structure and lattice dynamics

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Using combined neutron spectroscopy and first-principles calculations, we investigated the electronic structure and vibrational dynamics of the recently discovered class of ternary hydrides  $\text{Li}_4\text{Tt}_2\text{H}$  ( $\text{Tt}=\text{Si}$  and  $\text{Ge}$ ). In these compounds, all hydrogen atoms are located in a single type of  $\text{Li}_6$ -defined octahedral site. The  $\text{Tt}$  atoms form long-range  $\text{Tt-Tt}$  chains sandwiched between each  $\text{Li}_6$ -octahedra layer. The Li-H interactions are strongly ionic, with bond lengths comparable to those in  $\text{LiH}$ . Our density functional theory calculations indicate that Li atoms transfer their electrons to both H and  $\text{Tt}$  atoms.  $\text{Tt}$  atoms within the  $\text{Tt-Tt}$  chain are bonded covalently. The electronic density of states reveals that both hydrides exhibit metallic behavior. The observed vibrational spectra of these hydrides are in good overall agreement with the calculated phonon modes. There is evidence of dispersion induced splitting in the optical phonon peaks that can be ascribed to the coupling of H vibrations within the  $\text{Li}_6$ -octahedra layers.

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## I. INTRODUCTION

The Li-Si and Li-Ge binary phase diagrams have been well established.<sup>1-4</sup> Most of these phases show quite strong thermal stability and interesting structural diversity. Due to the relatively large cohesive energies of these lithium silicide and germanide phases, it was found that the strongly bound H atoms in  $\text{LiH}$  could be effectively destabilized by the addition of Si (Refs. 5 and 6) or Ge.<sup>7</sup> Consequently, the Si or Ge-doped  $\text{LiH}$  ( $\sim 12.5$  wt % H) dehydrogenates at a much lower temperature via the formation of various Li-Si or Li-Ge alloy phases concomitant with  $\text{H}_2$  release.

Interestingly, during dehydrogenation/hydrogenation studies of  $\text{LiH/Si}$  and  $\text{LiH/Ge}$  mixtures, two new isostructural, ternary hydride phases,  $\text{Li}_4\text{Si}_2\text{H}$  and  $\text{Li}_4\text{Ge}_2\text{H}$ , were formed.<sup>7</sup> To the best of our knowledge, H insertion into lithium silicides and germanides has not been reported previously. Thus, in contrast to the rich phase diagrams of Li-Si(Ge) binary systems,  $\text{Li}_4\text{Si}_2\text{H}$  and  $\text{Li}_4\text{Ge}_2\text{H}$  are the first and the only known compounds in the Li-Si(Ge)-H ternary systems.

We have recently reported the structure of these two hydride phases.<sup>7</sup> Figure 1 shows the refined crystal structure ( $Cmmm$ , No. 65) of  $\text{Li}_4\text{Ge}_2\text{H}$  and  $\text{Li}_4\text{Si}_2\text{H}$ . In these compounds, hydrogen atoms are located in the interstitial octahedral ( $2d$ ) sites exclusively defined by Li cations. These  $\text{Li}_6$  octahedra share corners with four other in-plane neighboring octahedra, forming  $\text{Li}_6$ -octahedral layers at  $h$  and  $h/2$  ( $h=0, 1, 2, \dots, n$ ) planes. All  $\text{Li}_6$  octahedra are identical, with three pairs of Li-H bonds along the  $a$ ,  $b$ , and  $c$  directions, respectively. Thus, there is only one crystallographic

site for interstitial hydrogen atoms. Such a  $\text{Li}_6$ -octahedral site is unique; in fact, it is so far the only reported octahedral interstitial site confined by single type of alkali metal in all known ternary hydride phases. Between two  $\text{Li}_6$ -octahedral layers, Ge or Si atoms align in a zigzag fashion, propagating

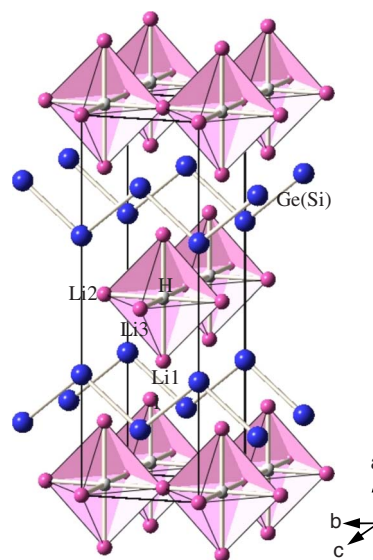


FIG. 1. (Color online) An off-[001] view of the orthorhombic  $\text{Li}_4\text{Tt}_2\text{H}$  crystal structure with centered octahedral interstices. The large blue and small pink spheres represent  $\text{Tt}$  ( $=\text{Si}$ ,  $\text{Ge}$ ) and  $\text{Li}$ , respectively, and the interstitial H atoms (small white) are centered in the shaded  $\text{Li}_6$  octahedra

along the **b** direction in the **c** basal planes. The Ge–Ge and Si–Si bond distances in these long-range  $-Tt-Tt-$  chains are much longer than the isolated  $Tt-Tt$  dimers in the binary Li- $Tt$  ( $Tt=Si$  and Ge) intermetallics, but comparable to those of the dimers in  $Ca_5Tt_3$  and  $Ca_5Tt_3H_x$ , and to those similarly bonded clathrate II network structures  $A_8A'_{16}Tt_{136}$  ( $A, A'$ =alkali metals,  $Tt=Si$  and Ge).<sup>8</sup>

The discovery of  $Li_4Si_2H$  and  $Li_4Ge_2H$  is a significant advance in our understanding of the Li-Si-H and Li-Ge-H ternary phase diagrams, which up to this point were in error. In addition to determining the structure, a thorough study of the interatomic bonding and stability of these previously unknown hydrides is necessary for a better understanding of their properties. A study of the hydrogen site is of particular interest to researchers dealing with the destabilization of the light-metal hydrides. In this paper, we present the results of neutron vibrational spectroscopy (NVS) and first-principles calculations on these ternary hydrides to better reveal the nature of their bonding interactions and the origin of their stabilities. Such information should contribute to a better overall understanding of hydride destabilization in LiH and similar light-metal hydride systems. The calculated electronic structures should also be useful for any potential applications involving their physical properties.

## II. MATERIALS AND EXPERIMENTAL METHODS

The  $Li_4Ge_2H$  and  $Li_4Ge_2D$  powder samples were synthesized via the following procedures. First, a 2:1 LiH (Alfa Aesar<sup>9</sup> 99.4%) and Ge (Alfa Aesar 99.999%) stoichiometric mixture was ball-milled with a Fritsch Pulverisette 7 planetary mill at 400 rpm for 30 min. The mixture was then heated and evacuated at 763 K in dynamic vacuum for 8–10 h to expel  $H_2$ . The products were then reground with an agate mortar and pestle in a He-filled glovebox. Finally, the hydrided or deuterided samples were prepared by direct reaction of the alloy with gas-phase  $H_2$  or  $D_2$  (99.999%) at 723–743 K under 2.5 MPa pressure. The compositions and structures of the products after each synthesis process were characterized using laboratory x-ray diffraction (Rigaku, D-MAX/UltimaIII) and neutron prompt-gamma activation analysis (PGAA) techniques.<sup>10</sup> Powders were wrapped in a Mo envelope and sealed in a stainless-steel tube during the high-temperature hydrogenation. All sample handling was performed in a He-filled glovebox to avoid oxidation reactions. The stoichiometry of the resultant  $Li_4Ge_2H$  sample was verified by PGAA. The deuterium content of the isostructured  $Li_4Ge_2D$  sample was confirmed gravimetrically.

The  $Li_4Si_2H$  and  $Li_4Si_2D$  powder samples were prepared using a modified procedure to maximize their formation. First, a LiH (Fluka, 97%)+Si (cleaved from electronic grade wafers) 1:1 stoichiometric mixture was ball milled (400 rpm for 1 h, see Ref. 6 for details) then evacuated at 773 K for 2–3 h to remove the hydrogen. Next, the LiSi alloy mixture was hydrided or deuterided to a stoichiometry of LiSiH or LiSiD with  $\approx 0.7$  MPa of  $H_2$  or  $D_2$  (99.999%) at 723 K. Again, hydrogen content was verified by PGAA. Finally, a portion of the H or D was removed from the sample to a final ratio of 0.25 H(D)/Li by controlled evacuation at

723 K followed by annealing for 8–9 d at 723 K in a sealed stainless-steel sample tube. The final sample composition was approximately  $Li_4Si_2H(D)+2Si$ . The presence of excess Si was found to be necessary to promote  $Li_4Si_2H(D)$  formation instead of LiH(D).

The NVS measurements were performed at the NIST Center for Neutron Research (NCNR) using the BT-4 Filter-Analyzer Neutron Spectrometer<sup>11</sup> with the Cu(220) monochromator under conditions that provided full-width-at-half-maximum energy resolutions of 2–4.5% of the incident energy over the range probed. PGAA measurements were performed at the NCNR with the NG-6 high-resolution  $\gamma$ -ray spectrometer.

First-principles calculations were performed within the plane-wave implementation of the generalized gradient approximation to density functional theory (DFT) using the PWSCF package.<sup>12</sup> We used a Vanderbilt-type ultrasoft potential with Perdew-Burke-Ernzerhof exchange correlation. A cutoff energy of 480 eV and a  $6 \times 6 \times 8$   $k$ -point mesh were found to be enough for the total energy to converge within 0.5 meV/atom and 0.005 eV/Å. Structure optimizations were performed with respect to lattice parameters and atomic positions. The phonon calculations were conducted with the optimized structure using the supercell method with finite difference.<sup>13,14</sup>

## III. RESULTS AND DISCUSSION

According to our previous neutron-diffraction-based structural results for the deuterided samples,<sup>7</sup> the three different Li–D bond lengths associated with the  $Li_6$  octahedra (i.e., Li1-D, Li2-D, and Li3-D in Fig. 1) were in the range of 1.88–2.09 Å. These values are comparable to that in pure LiH (Li–H  $\sim 2.031$  Å), indicating quite strong Li–H bonding. Also, the nearest Li- $Tt$  ( $Tt=Si$  and Ge) distances are significantly lengthened compared to those in the various Li-Ge and Li-Si intermetallic binaries,<sup>15–19</sup> indicating the weakened interactions between Li and  $Tt$  atoms. Therefore, as we previously proposed, it is the strong Li–H bonding that likely stabilizes these ternary hydride phases. In order to better understand the bonding nature and local bonding configuration, we performed first-principles DFT calculations on these phases. We first optimized the  $Cmmm$  crystal structures. The relaxed atomic positions agreed well with our refined values for  $Li_4Si_2D$  and  $Li_4Ge_2D$ . Figure 2 plots the total electron densities of states (DOSs) and their projections on the different atomic sites for the  $Cmmm$  structures of  $Li_4Si_2D$  and  $Li_4Ge_2D$ . Both hydrides show similar electronic band structures. The prominent ( $\approx 1$ –1.5 eV width) low-energy feature observed in the total DOS (centered about 5.2 eV below the Fermi energy,  $E_F$ ) corresponds to Li–H bands in both hydrides. Only Li 2s states participate in the H-metal bonding. Again, consistent with our previous suggestion based on diffraction results,<sup>7</sup> the strong Li–H interaction plays a crucial role in stabilizing these ternary hydrides, due to its lowering of the energy of the Li  $s$  states below the Fermi level of the hydrides. The total DOS band structure at higher energy is governed by the strong hybridization of Si 3p or Ge 4p states. The Li 2s states are more delocalized, which results in

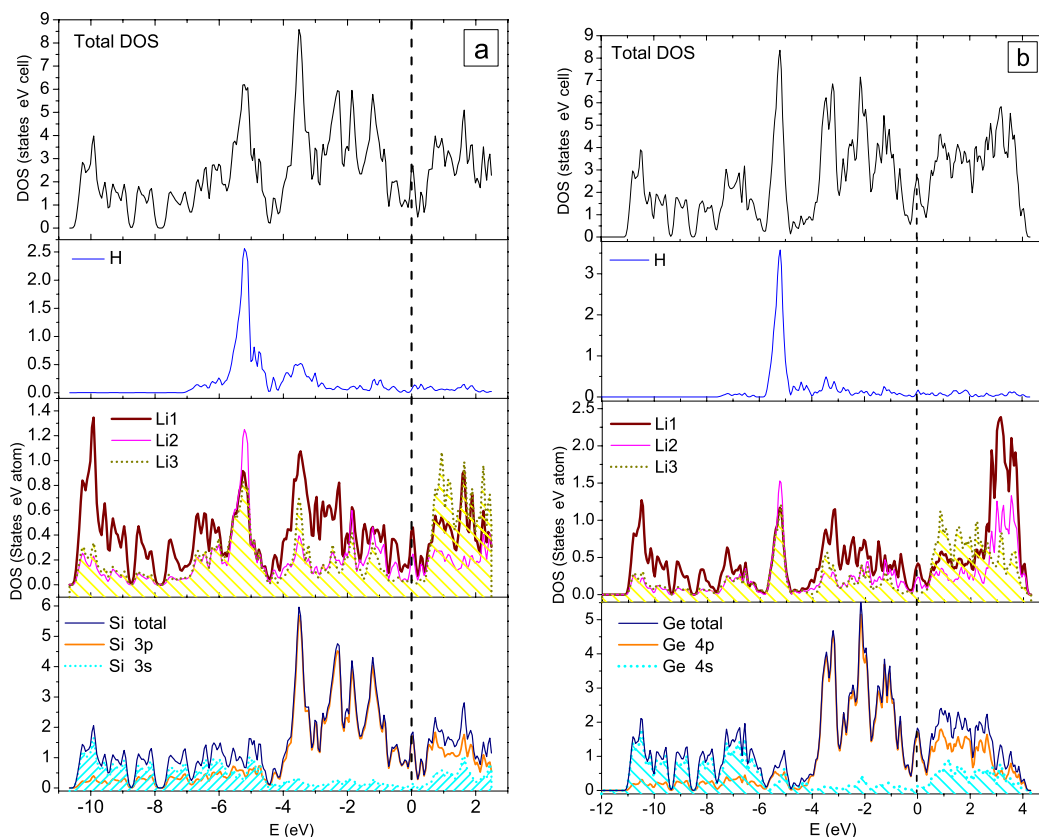


FIG. 2. (Color online) Total electronic DOS of (a)  $\text{Li}_4\text{Si}_2\text{H}$  and (b)  $\text{Li}_4\text{Ge}_2\text{H}$  and projection around the different atomic sites.  $E_F$  is taken as the zero of energy and shown as the dashed line.

much broader bands of lower DOS. The Si  $3p$  (Ge  $4p$ ) contributions to DOS at and above  $E_F$  are larger than those of the Li  $s$  state in both hydrides.  $\text{Li}_4\text{Si}_2\text{H}$  and  $\text{Li}_4\text{Ge}_2\text{H}$  exhibit metallic behavior due to the finite electron states at the Fermi level  $N(E_F)$ , which is dominated by the Si  $3p$  or Ge  $4p$  state. Figure 3 shows five characteristic charge-density maps [i.e., (100) and (002) planes including Li and H, (001) including Li and Si, and (010) and (010) planes including Li, Si, and H]. From Fig. 3, it is clear that electron charge from Li atoms is almost fully transferred to H and Si atoms as there is nearly no electron density left at Li sites. The highest charge density is situated at each H-atom site, indicating very strong H-Li interactions that are primarily ionic. Some charge transfer from Li to Si atoms also indicates an ionic contribution to the bonding between them. The large overlap of the electron clouds between neighboring Si shows strong covalent bonding within the Si-Si chains. This is consistent with the strong hybridization as observed in the DOS (Fig. 2). Therefore, the bonding in  $\text{Li}_4\text{Si}_2\text{H}$  and  $\text{Li}_4\text{Ge}_2\text{H}$  is a mixture of ionic and covalent characters. The charge densities in the regions between Li, H, and Si chains is rather low, implying the bonding between  $\text{Li}_6$ -octahedral layers and Si-Si chains is directional but not metallic. Similar charge-density plots were also obtained in  $\text{Li}_4\text{Ge}_2\text{H}$ .

To gain additional insight into the nature of bonding in these ternary hydrides, we studied the phonon density of states of these ternary hydrides using neutron vibrational spectroscopy. Figure 4 illustrates the NV spectra of

$\text{Li}_4\text{Si}_2\text{H(D)}$  and  $\text{Li}_4\text{Ge}_2\text{H(D)}$  at 10 K, respectively. The spectrum for  $\text{Li}_4\text{Si}_2\text{H}$  displays three distinct peaks at 84.1, 100.0, and 123.4 meV. Such spectral features are consistent with the refined crystal structure possessing a single H site, since three normal-mode vibrations generally accompany one type of hydrogen site. The deuteride spectrum is similar but downshifted in energy by roughly a factor of  $1/\sqrt{2}$  due to the doubled isotopic mass for D compared to H. The spectra of the germanide hydrides are analogous to those of their silicide counterparts, with three main phonon bands at around 86.9, 99.0, and 116.3 meV for  $\text{Li}_4\text{Ge}_2\text{H}$  and 61.4, 70.6, and 83.7 meV for  $\text{Li}_4\text{Ge}_2\text{D}$ .

To interpret the spectra and correlate the observed phonon density of states with the refined crystal structures, we performed first-principles phonon calculations. The phonon calculations were performed with the optimized structure using the supercell method with finite difference.<sup>14</sup> A cell of  $2a \times 2b \times 2c$  was used and the full dynamical matrix was obtained from a total of 36 symmetry-independent atomic displacements (0.01 Å). The NV spectra of  $\text{Li}_4\text{Ge}_2\text{H}$  and  $\text{Li}_4\text{Si}_2\text{H}$  were computed for a  $10 \times 10 \times 10$   $q$  point grid within the incoherent approximation with the instrumental resolution taken into account.<sup>20</sup> The primitive cells of  $\text{Li}_4\text{Si}_2\text{H}$  and  $\text{Li}_4\text{Ge}_2\text{H}$  contain seven atoms giving rise to a total of 21 phonon branches ( $2A_g + 2B_{1g} + 5B_{1u} + 2B_{2g} + 5B_{2u} + 5B_{3u}$ ). Inspection of the eigenvectors allows the characterization of the modes. The NV spectrum is dominated by H-atom displacements. Phonon spectra largely associated

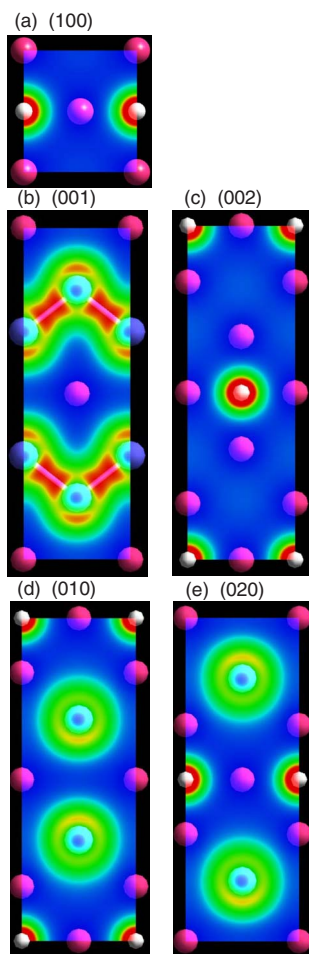


FIG. 3. (Color online) Characteristic charge-density maps on (a) (100), (b) (001), (c) (002), (d) (010), and (e) (020) planes. The values of the contours in all maps are from 0 to  $0.57 e/\text{\AA}^2$ . The atoms (H, small white; Li, medium pink; Si, large blue spheres) on the corresponding crystallographic planes are also shown underneath the transparent charge-density maps for clarity.

with the metal-atom displacements (peaks between 0 and 30 meV) were not measured. Figure 5 compares the calculated phonon modes with the observed NV spectra. Calculations considering 1-phonon and (1+2)-phonon contributions to NV spectra yield similar spectra in the measured energy range. Three phonon modes in the range of 75–135 meV in the NV spectra of  $\text{Li}_4\text{Si}_2\text{H}$  and  $\text{Li}_4\text{Ge}_2\text{H}$  originated from H atoms in  $\text{Li}_6$ -octahedral sites, with increasing phonon-mode energies associated with H vibrations along the different H–Li bond axes with decreasing bond lengths, respectively (i.e., increasing bonding strengths), as expected.

From Fig. 5, the calculated phonon modes for these ternary hydrides agree reasonably well overall with the observed NV spectra. The lowest and highest phonon peaks correspond to the H vibrations along the longest and shortest Li–H bonds within each  $\text{Li}_6$  octahedron. Phonon modes at 100.0 meV ( $\text{Li}_4\text{Si}_2\text{H}$ ) and 99.0 meV ( $\text{Li}_4\text{Ge}_2\text{H}$ ) originate from the H vibrations along the Li1-H direction. The measured spectra showed some significant weaker sidebands for the lowest and highest vibrational peaks. Since our calculations give single sharp peak while the neutron data show a shoulder on each peak for the hydrogen modes at the Li-octahedral center, it is quite possible that the  $2 \times 2 \times 2$  supercell used in our calculations is not large enough to capture all possible dispersion of the hydrogen phonon modes. It is also possible that in real materials some of the Li octahedra may have Li vacancy as a defect which could give slightly different phonon modes and show up as a shoulder in the measured spectrum. The middle vibrational peaks in both spectra do not show evidence of dispersion in the phonon branches and can be well reproduced by first-principles calculations. We believe that the indication of dispersion of the phonon modes can be ascribed to the “sandwiched” structure characteristic of these hydride phases. From the crystal structure (Fig. 1), each  $\text{Li}_6$  octahedron shares corners (Li2 and Li3) with four neighboring octahedra within the **a** basal planes and leaves the other two vertices (Li1) along the **a** direction unshared. Therefore, vibrations of the H atom in each  $\text{Li}_6$  octahedron along the **b** and **c** directions would be more affected by the motions of other H atoms in the neighboring

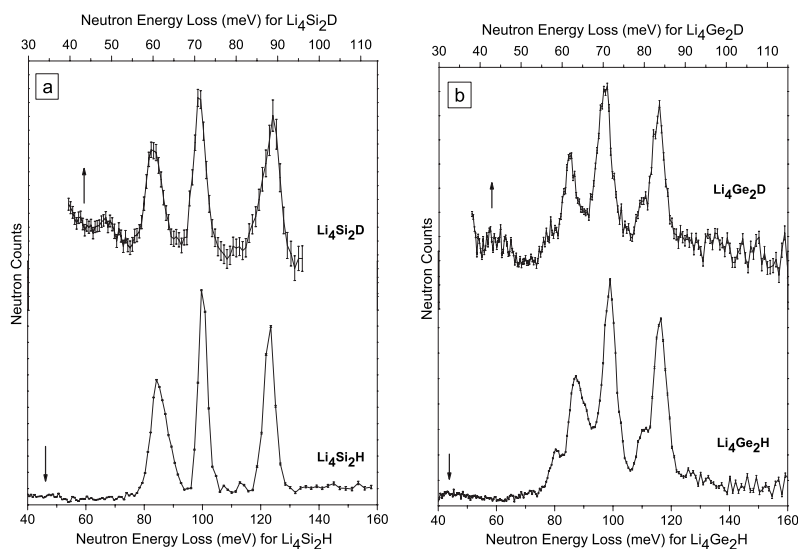


FIG. 4. NV spectra of (a)  $\text{Li}_4\text{Si}_2\text{H(D)}$  and (b)  $\text{Li}_4\text{Ge}_2\text{H(D)}$  at 10 K. The ratio of corresponding energy-loss scales for hydrides and deuterides is  $\sqrt{2}$ . The spectra for hydrides and deuterides are plotted using the bottom and the top x axes, respectively.



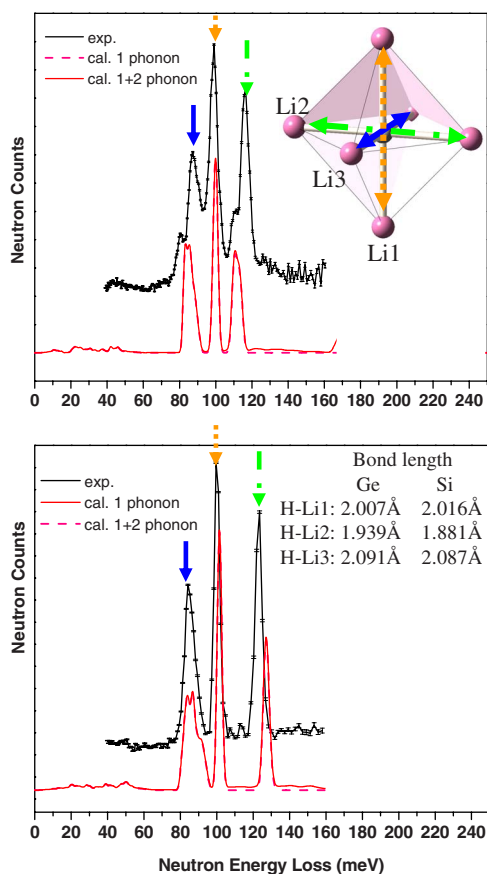


FIG. 5. (Color online) Comparison of observed NV spectra of  $\text{Li}_4\text{Si}_2\text{H}$  (bottom panel) and  $\text{Li}_4\text{Ge}_2\text{H}$  (top panel) with the calculated spectra. The inset schemes the assigned H phonon modes corresponding to their observed peaks in the NV spectra (solid, dot, and dash-dot arrows indicate the H phonon modes in  $\text{Li}_6$ -octahedron and the corresponding observed peaks in NV spectra, respectively), which are well correlated with the Li-H bond lengths.

octahedra and most likely couple with these motions. Consequently, the coupling of vibrations along these two directions within the octahedral layers can induce dispersion of the corresponding phonon modes. The vibrations of H atoms along the  $\mathbf{a}$  direction will not be so affected because the octahedral H sites are interrupted by Si-Si or Ge-Ge chains along this direction. As a result, the middle peaks in both spectra are sharp features without evidence of dispersion.

The formation of the Li-Si-H and Li-Ge-H ternaries is surprising as they have not been previously identified in spite of the well-established and rich Li-Si and Li-Ge phase diagrams. Notably,  $\text{Li}_2\text{Si}$  and  $\text{Li}_2\text{Ge}$ , which possess the same Li/Si(Ge) ratios as in the ternary hydrides, are not, by them-

selves, known stable binary Li-Si(Ge) phases. Thus, it is important to understand why these particular ternary hydride phases can exist and be stable at room temperature. As we have pointed out, these ternaries exhibit an unusual structure with a unique  $\text{Li}_6$ -octahedral hydrogen site and long-range Si-Si (and Ge-Ge) two-dimensional chains.

Our electronic structure study reveals a strong ionic bonding between Li and H, which is primarily responsible for the stabilization and existence of these ternaries, in contrast to the lack of “ $\text{Li}_2\text{Si}$ ” and “ $\text{Li}_2\text{Ge}$ ” phases in prior literature. Our results do not necessarily indicate that these ternaries are more stable than the known  $\text{Li}_x\text{Si}_y$  or  $\text{Li}_x\text{Ge}_y$  binaries. Yet, the recognition of these ternary hydrides certainly advances our understanding of the current Li-Si-H and Li-Ge-H phase diagrams, and more importantly, the mechanism and the reaction path of hydride destabilization in these and perhaps other alloy hydrides.

#### IV. SUMMARY

Using combined neutron vibrational spectroscopy and first-principles calculations, we investigated the electronic structure and lattice dynamics of a new class of ternary hydrides  $\text{Li}_4\text{Ti}_2\text{H}$  ( $\text{Ti}=\text{Si}$  and  $\text{Ge}$ ). Our calculations confirmed that the formation of these new ternary hydrides is stabilized by the presence of strong Li-H bonding. In these compounds, there is only one type of crystallographically distinct  $\text{Li}_6$ -octahedral H interstitial site.  $\text{Ti}$  atoms form long-range  $\text{Ti-Ti}$  chains sandwiched between Li-octahedra layers. From our DFT calculations, Li atoms transfer their electrons to both H and  $\text{Ti}$ . Li-H exhibits strong ionic bonding.  $\text{Ti}$  atoms accept electrons from Li and are covalently bonded with their neighbors within the  $\text{Ti-Ti}$  chains. The calculated total DOS indicates that both hydrides are metals. The observed vibrational spectra of these hydrides are in good overall agreement with the calculated phonon density of states. Splitting of the in-plane H vibrational peaks was observed, indicating dispersion of these lattice modes that can be ascribed to the coupling of H vibrations within the  $\text{Li}_6$ -octahedra layers.

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