Neutron vibrational spectroscopic evidence for short H···H contacts in the RNiInH$_{1.4}$; 1.6 ($R =$ Ce, La) metal hydride

Ryan A. Klein$^{ab}$*, Rafael Balderas-Xicohténcatl$^c$, Jan Petter Maehlen$^d$, Terrence J. Udovic$^{b,e}$, Craig M. Brown$^{b,f}$, Robert Delaplane$^d$, Yongqiang Cheng$^c$, Roman V. Denys$^d$, Anibal J. Ramirez-Cuesta$^a$, Volodymyr A. Yartys$^{b,***}$

$^a$Materials, Chemical, and Computational Science Directorate, National Renewable Energy Laboratory, Golden, CO 80401, USA
$^b$NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
$^c$Oak Ridge National Laboratory, Neutron Sciences Division, Spallation Neutron Source, Oak Ridge TN 37831, USA
$^d$Institute for Energy Technology, 2027 Kjeller, Norway
$^e$Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742, USA
$^f$Department of Chemical Engineering, University of Delaware, Newark, DE 19716, USA

1. Introduction

Hydrogen is emerging as a key renewable energy carrier in the push towards a decarbonized energy economy [1]. Yet, the widespread adaptation of hydrogen in energy systems is hindered by a lack of suitable storage materials for both stationary and mobile applications [2,3]. One promising class of materials for hydrogen storage applications are the metal hydrides, which chemisorb molecular hydrogen and store the H atoms in the interstices of the metal lattice [4]. Currently, the best metal hydride materials suffer from low reversible hydrogen storage capacities at operationally relevant conditions [5,6]. Although the volumetric capacity in metal hydrides is high—exceeding that of liquid H$_2$ in many cases [7]—it is fundamentally limited based on an empirical rule known as the Switendick-Westlake criterion [8,9]. This criterion defines a minimum threshold distance between the hydrogen atoms within structures of metal hydrides of $\approx 2.1$ Å. This minimum threshold distance arises from H···H coulombic repulsion [10]. The volumetric capacity of H in metal hydrides at operationally relevant conditions can be increased if the Switendick-Westlake criterion could be rationally overcome to increase the volumetric density of H atoms in the metal lattice.

Powder neutron diffraction (PND) studies of intermetallic hydrides have shown that, in practice, the number of available interstices is significantly higher than the number of occupied interstices. As the hydrogen loading increases, the available interstices are either...
filled statistically, with occupancies not exceeding ½, or they are filled in an ordered way. For an ordered filling of the sites, the thermodynamically most favorable interstices that first become occupied by H atoms can block nearby sites from filling, via coulombic interactions. Consequently, one important observation is that tetrahedral interstices which share a common face, are never simultaneously filled by H atoms because the distances between their centers are below 2.1 Å, in accordance with the Switendick-Westlake criterion. One typical example is the cubic AB₂ Laves‐phase family of intermetallic compounds [11,12]. This structure type contains 17 interstitial sites per AB₂ unit, including 12 A₂B₃ sites, 4 AB₃ sites, and 1 B₄ site. Yet, the maximum observed stoichiometry of the hydride is 6 absorbed H atoms per AB₂ unit, as in Zr₂V₆ (3 Zr₂V₂ + 3 ZrV₂ sites occupied) [13–15]. At lower hydrogen content, H atoms ordered superstructures, as in ZrV₂D₆ (4 ZrV₂ sites / Zr₂V₂ unit occupied) [16]. Hydrogen ordering results in H–H contacts exceeding 2 Å.

Very few known compounds to date have displayed unambiguous H–H contacts closer than 2 Å. These include Th₂AlH₆ [17–20] and a series of RNiInHₓ hydrides (R = La, Ce, Nd, Pr) [21–27]. The RNiInHₓ (0 ≤ x ≤ 1.6) compounds crystallize in the hexagonal R₂Zn space group (hexagonal ZrNiAl structure type) with hydrogen (deuterium) atoms preferentially filling the R₃Ni tetrahedra (4h crystallographic sites) below x = 1.33. Prior PND studies of the deuterided RNiInDₓ compounds [28] indicated that, as the deuterium loading increases above x = 0.67, both R₃Ni interstices of the Ni₅R₃ trigonal bipyramids begin to become simultaneously occupied to form close D–D contacts in the metal lattice. Such close pairings are ideally maximized at full R₃Ni-site occupation (x = 1.33). These D–D contact distances are 1.635(8) Å, 1.606(6) Å, 1.562(9) Å, and 1.570(8) Å for LaNiInD₁₂, CeNiInD₁₂, NdNiInD₁₂, and NdNiInD₁₄, respectively (values in parentheses here and throughout represent 1σ) [28]. In the La congener, as the loading increases above x = 1.33, an additional interstice, the 12i Wyckoff site located within La₃NiIn₂ distorted octahedra, becomes populated (although there are indications that these sites can begin to fill before the 4h tetrahedral sites are fully occupied). Fig. 1 shows the structure of LaNiInD₁₆₃ and highlights the tetrahedral 4h (blue polyhedra) and octahedral 12i (red polyhedra) sites in the structure. As the deuteride concentration increases to x = 1.63, the D–D contact length increases to 1.715(1) Å [29].

First-principles density functional theory (DFT) investigations of the Rh₃NiHₓ compounds revealed a possible mechanism enabling the close H–H pairs. Electron localization function calculations showed that, along the Ni–H chains aligned in the (001) direction, the electron density is localized between the Ni and H atoms to form an H–Ni–H bonded fragment with significant electron density polarization directed towards the In and Ni atoms (i.e. away from the La₃ face) [30–32]. It was suggested that the shared R₃ faces joining adjacent R₃Ni tetrahedra effectively screen the H–H coulombic repulsion, thus enabling the close hydrogen contacts. Yet, further experimental characterization of these materials is still highly desirable to validate the DFT methodology and develop a more precise understanding of the Ni–H, R–H, and possible H–H interactions. A deeper understanding of these interactions may help to further shed light on the mechanism by which these compounds violate the Switendick-Westlake criterion. As such, spectroscopic measurements coupled with DFT phonon calculations are needed to corroborate and enhance our current understanding of the bonding interactions in the RNiInₓ metal hydrides.

Here we present neutron vibrational spectroscopy (NVS) measurements coupled with DFT calculations for the ternary hydrides CeNiSnHₓ CeNiSnHₓ and CeNiSnDₓ. These materials share some local structural similarities with the RNiInₓ compounds, however they do not show the crystallographic or spectroscopic signatures of close H–H contacts.

2. Experimental section

2.1. Synthesis of RNiIn and CeNiSn based hydrides/deuterides

The parent RNiIn intermetallic compounds were prepared by arc melting mixtures of the compact pieces of pure elements (purity > 99.9%) followed by annealing at elevated temperatures in an evacuated quartz ampoule according to previously established procedures [28,29,33]. Typically, the single pieces of the annealed samples were transferred to a Sieverts-type system with an autoclave placed in a furnace, activated at high temperatures (573–623 K), and then exposed for a specific period to gaseous H₂/D₂ at an appropriate temperature and pressure. For LaNiIn, approximately 1.4 g was exposed to 0.5 MPa H₂ at room temperature to form LaNiInH₁₂. LaNiInH₁₂ was formed from LaNiInH₁₂ by removal of the required amount of H₂ outgassed from the sample at 473 K followed by cooling to room temperature.

For CeNiSn (TiNiSi-type orthorhombic structure), hydrogenation at 523 K under 5 MPa of H₂ gas has been found by X-ray diffraction (XRD) to yield the dihydride CeNiSnH₂ (hexagonal, filled ZrBeSi-type structure) (in house studies and [34]). Hydrogen evacuation of the dihydride at this same temperature leads to decomposition towards the monohydride CeNiSnH (orthorhombic, deformed TiNiSi-type structure). In both hydrides, the metal sublattice has a similar structure to the original intermetallic alloy, however, with different degrees of deformation. Here, CeNiSnH₂ was prepared by heating 6 g of CeNiSn at 500 K under 3.5 MPa H₂ gas for 20 h. An analogous procedure using D₂ yielded CeNiSnD₂. Finally, a roughly equimolar mixed-phase monohydride + dihydride CeNiSnH₁.₄₃ sample (53% orthorhombic CeNiSnH + 47% hexagonal CeNiSnH₂ based on PND results) was prepared by heating 6 g of CeNiSn at 650 K under 0.4 MPa H₂ gas for 4 h.

![Fig. 1. Two unit cells of the hexagonal R2Zn crystal structure for LaNiInD₁₆₃ are shown stacked in the (001) direction. Octahedral and tetrahedral coordination environments for the D atoms are highlighted as the red and blue polyhedra, respectively. For clarity, only one column of octahedral polyhedra is shown. The Ni–D–Ni–D–Ni–D–Ni chains containing the close D–D contacts between neighboring LaNi tetrahedral sites run in the (001) direction along the La₃Ni chains. The close D–D contact between adjacent La₃Ni tetrahedra is highlighted by a bold scale bar, indicating a separation of 1.715(1) Å. Gray, green, pink, and blue spheres depict Ni, La, In, and D atoms, respectively, while partial shading denotes occupancy. Figure adapted from reference [29].](image-url)
2.2. Powder neutron diffraction measurements of CeNiSnH$_x$

PND patterns for samples of CeNiSnH$_x$, CeNiSnD$_2$, and CeNiSnH$_{1.43}$ were collected at 295 K using the high-resolution R2D2 instrument ($\lambda = 1.551(1)$ Å, $\phi$ step = 0.05°) at the R2 Reactor at the Studsvik Neutron Research Laboratory, Uppsala University, Sweden (Figs. S6–S8).

The instrument calibration parameters and wavelength of the neutron beam were determined by a least-squares fit for diffraction data collected for the standard reference materials; Si, NIST 640c and Al$_2$O$_3$, NIST 676. The samples were loaded in a vanadium sample can (inner diameter = 6 mm). The Pawley [35] and Rietveld [36] refinements of the structure parameters were performed with the GSAS/EXPGUI program package [37].

2.3. Neutron vibrational spectroscopic measurements

The neutron vibrational spectra for the LaNiInH$_{0.67}$ and LaNiInH$_{1.6}$ compounds were collected at the National Institute of Standards and Technology Center for Neutron Research (NCNR) using the BT-4 Filter Analyzer Neutron Spectrometer (FANS) [38]. To collect these spectra, horizontal 20° collimations were used before and after the Cu(220) monochromator to collect higher-resolution data in a neutron energy loss range from 33 meV (≈ 266 cm$^{-1}$) to 160 meV (≈ 1290 cm$^{-1}$). Additional lower-resolution spectra in a neutron energy loss range from 33 meV (≈ 266 cm$^{-1}$) to 256 meV (≈ 2064 cm$^{-1}$) were collected by employing horizontal 60° and 40° collimations before and after the monochromator (Figs. S1, S2 in the Supplemental Information document). Because of the large neutron absorption cross section of In (≈ 194 b) [39], the samples were measured as flat plates in a reflectance geometry to enhance scattering signal.

The neutron vibrational spectra for CeNiInH$_{1.4}$ and for the CeNiSnH$_x$ compounds were collected using the high-resolution broadband TOSCA spectrometer at the pulsed neutron source of ISIS at the Rutherford-Appleton Laboratory in Chilton, the United Kingdom (Figs. 53–55). In an inert atmosphere, the samples were loaded into flat aluminum sample holders and data were collected at 20 K.

2.4. Density functional theory calculations

Density Functional Theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP) [40]. The calculations used the Projector Augmented Wave (PAW) method [41,42] to describe the effects of core electrons, and Perdew-Burke-Ernzerhof (PBE) [43] implementation of the Generalized Gradient Approximation (GGA) for the exchange-correlation functional. The energy cutoff was 600 eV for the plane-wave basis of the valence electrons. The total energy tolerance for the electronic energy minimization was 10$^{-8}$ eV. After structural optimization, a supercell (2×2×3) of the unit cell except for CeNiSnH, for which it was 3×3×2) was used for the phonon calculations. The vibrational eigen-frequencies and modes were then calculated by solving the force constants and dynamical matrix using Phonopy [44]. The OCLIMAX software [45] was used to convert the DFT-calculated phonon results to the simulated NV spectra. The DFT calculations for all spectra were conducted using both lattice-dynamics (LD) and molecular-dynamics (MD) approaches. The simulated spectra based on the calculations arise from sampling the entire Brillouin zone. Based on the calculated Γ-point phonons, animations depicting the

atomic motion for each mode were generated and these animations were used to facilitate mode assignments for the measured spectra. These animations—included as phonon files in the Supplementary Material Data—can be visualized using the Jmol software package [46]. For LaNiInH$_{0.67}$, an ordered singlet model was used for the calculations in which each Ni atom was paired with one H atom such that the Ni–H bonds all pointed uniformly in the positive c-axis crystallographic direction. An additional doublet model which assumed an ordered structure of half-filled 4$h$ Wyckoff positions, but with only H–Ni–H pair configurations present, was also used for the calculations. Since the simulated spectrum using this model resulted in poor agreement with the measured spectrum and its DFT-predicted potential energy (per H atom) was 0.32 eV higher than that for the singlet structure, it was not considered further. As such, the results discussed below are based on the calculations performed using the ordered singlet model for LaNiInH$_{0.67}$. In all LD simulations, the DFT calculated energy bands are scaled to align with the corresponding peak positions in the measured INS spectra, and the scaling constant ranges from 0.9 to 1.1 (mostly within 1% ± 5%). In addition, MD simulations were performed to better understand anharmonic effects. For example, strong anharmonicity is observed for the three rattling modes of the hydrogen atom at the 12$I$ octahedral site in LaNiInH$_{1.6}$. The peak positions are nicely reproduced by the MD simulation whereas they are substantially overestimated by the LD simulation. On the other hand, the MD approach tends to produce broader peaks, and the LD simulation reproduces the peak profile (such as the splitting) better, as observed in Fig. 2. As such, we use the animations associated with the calculations for the LaNiInH$_{0.67}$ compound to describe the split modes centered near 92 meV in the measured spectrum for LaNiInH$_{1.6}$. For the octahedral H modes in the measured spectrum for LaNiInH$_{1.6}$, we use the animation for the corresponding feature in the simulated spectrum for LaNiInH$_{1.6}$. Lattice dynamics DFT calculations were sufficient for the CeNiSnx compounds.

3. Results and discussion

3.1. Neutron vibrational signatures of close H–H contacts

The neutron-fast-background-corrected vibrational spectra for LaNiInH$_x$ (x = 0.67, 1.6) and CeNiSnH$_{1.4}$ are shown in Fig. 2 along with the simulated spectra for LaNiInH$_x$ (x=0.67, 1.33, 1.6) and CeNiSnH$_{1.6}$. Below we detail the features in each spectrum, and, aided by the DFT calculations, we give assignments for each observed mode. The mode positions and assignments are tabulated in Table 1. Based on the calculated animations, we identify dynamic motions for the H atom at the 4$h$ Wyckoff sites which are either orthogonal to the basal $R_3$ plane in the $R_3Ni$ tetrahedra (Ni–H stretching modes) or parallel to the basal plane (which we term ‘bending’ and ‘rocking’ modes). We note that, in true molecular bending and rocking modes, the Ni–H distances would be constant, and the H atoms would move in a sweeping motion. Here, the H atom moves parallel to the $R_3$ face, such that the Ni–H distances vary slightly as the H atoms vibrate. As such, we use the terms ‘bending’ and ‘rocking’ in the following discussion as purely descriptive terms to differentiate between the types of motions of the H atoms within a single H–Ni–H bonded fragment, and the quotation marks around the terms will not be used hereafter.

The crystal structure of LaNiInD$_{0.48}$ was shown to contain one occupied hydrogen atom position, the 4$h$ site, with an occupancy of 0.36 such that there are no close D–D contacts in violation of the Switendick-Westlake criterion at this loading concentration [26]. The neutron vibrational spectrum for the analogous LaNiInH$_{0.67}$ contains two narrowly split features at neutron energy loss values of 120.7(5) meV (≈ 974 cm$^{-1}$) and 126.9(5) meV (≈ 1024 cm$^{-1}$) and a broad band extending from ≈ 80 to 106 meV (≈ 645 cm$^{-1}$ to
The measured spectra. Note that the LD-based spectrum shown beneath the measured blue curves, respectively, for the La congener are plotted with arbitrary offsets below (Ni–H) and Table 1.

The neutron vibrational spectra for LaNiInH$_x$ are depicted by the gray curves. LD-based and MD-based simulated spectra (red and green curves, respectively) for the La congener are plotted with arbitrary offsets below (Ni–H) and Table 1.

Table 1

<table>
<thead>
<tr>
<th>Hydride</th>
<th>d(Ni–H) (Å)</th>
<th>d(H–H) (Å)</th>
<th>(Ni–H) ‘bending’ (meV)</th>
<th>(H–Ni–H) ‘rocking’ (meV)</th>
<th>$\sigma$(H–Ni–H) ‘bending’ (meV)</th>
<th>$\delta$(H–Ni–H) ‘bending’ (meV)</th>
<th>$\nu$(Ni–H) stretching (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNiInH$_{0.67}$</td>
<td>1.68(1)$^c$</td>
<td>–</td>
<td>120.7(5), 126.9(5)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>~80–106 (band)</td>
</tr>
<tr>
<td>CeNiSnH</td>
<td>1.62(6)</td>
<td>2.66(1)</td>
<td>102.0(3), 118.9(1)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>156.2(1)</td>
</tr>
<tr>
<td>LaNiInH$_{1.6}$</td>
<td>1.49(4)$^c$</td>
<td>1.71(5)$^c$</td>
<td>87.68(9)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>209, 230 (calc.)</td>
</tr>
<tr>
<td>CeNiInH$_{1.4}$</td>
<td>1.50(3)$^c$</td>
<td>1.60(6)$^c$</td>
<td>88.29(4)</td>
<td>–</td>
<td>97.00(7)</td>
<td>–</td>
<td>140.63(4)</td>
</tr>
<tr>
<td>CeNiInH$_2$</td>
<td>1.63(3)$^c$</td>
<td>2.78(1)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

‘Bending’ and ‘rocking’ refer to H || R3 motion in the R3Ni tetrahedra as described in the text. Values in parentheses indicate ± 1σ.

$^a$ Contact distances for LaNiInH$_{0.67}$ and CeNiInH$_{1.4}$ based on crystal structures for LaNiInD$_{0.68}$ and CeNiInD$_{2.26}$, respectively [28].

$^b$ Contact distances for LaNiInH$_{1.6}$ based on the crystal structure for LaNiInD$_{1.63}$ [29].
bipyradyim, move out-of-phase with each other. In contrast, the bending mode at 97.0(3) meV corresponds to degenerate correlated bending motions of the (H–Ni–H) moieties which are in-phase both between and within the NiLaNiH$_2$ molecules in the (001) crystallographic direction. The close H–H atoms in adjacent LaNi$_3$H$_5$ tetrahedra move in-phase with each other (see phonon files included with the Supplemental Materials). Hence it is clear that the narrowly split bending modes at 120.7(5) meV and 126.9(5) meV in LaNiInH$_3$ are significantly red-shift and further split in LaNiInH$_3$.S as the close H–H contacts form.

The simulated spectrum for LaNiInH$_3$.S also contains the in-phase and out-of-phase $\nu_{sym}$(Ni–H) symmetric stretching modes at significantly higher neutron energy loss values of ~209 meV ($\approx$ 1690 cm$^{-1}$) and ~231 meV ($\approx$ 1830 cm$^{-1}$), respectively. For the in-phase modes, the close H–H atoms vibrate with each other whereas for the higher-energy mode, these atoms vibrate against each other. These values are out of the measured spectral window for the high-resolution measurement shown in Fig. 2 and are unfortunately not well resolved by the higher-energy, low-resolution measurement shown in Fig. S2.

Weaker modes at 52.1(1) meV, 122.0(5) meV, and 158.6(5) meV correspond to the three normal-mode vibrations of the hydrogen atoms filling the LaNiIn$_2$ distorted octahedra. The modes at 52.1(1) meV and 158.6(5) meV represent orthogonal vibrations of the H atom within the equatorial LaNi$_2$ plane, whereas the mode at 122.0(5) meV corresponds to motions of this atom in the $c$-axis direction along the In–H–In axis. These motions are associated with minimal accompanying motion from the hydrogen atoms at the 4$h$ site (see phonon files included as Supplemental Materials).

The measured spectrum for CeNiInH$_3$.S is also shown in Fig. 2. The two features indicative of close H–H contacts are also prominent in this spectrum. The features for the (H–Ni–H) rocking and $\delta$(H–Ni–H) bending modes appear at neutron energy loss values of 88.29(4) meV ($\approx$ 712 cm$^{-1}$), and 97.00(7) meV ($\approx$ 782 cm$^{-1}$), respectively. Given the structural similarity in the R$_3$Ni (R = La, Ce) tetrahedra between LaNiInH$_3$.S and CeNiInH$_3$.S, these modes remain at nearly the same energy loss values between the two compounds. The slight differences in energy for the modes may arise from the slightly longer La–Ni bonds in LaNiInH$_3$.225 (3.2445(8) Å) compared to CeNiInH$_3$.236 (3.2128(11) Å) [28] leading to slightly less confined H atoms and therefore slightly lower energy modes in the La compound. Unfortunately, similar to the LaNiInH$_3$.S case, the $\nu$(H–Ni) stretching frequencies for CeNiInH$_3$.S above 200 meV are also not well resolved in the higher-energy, high-resolution measurement shown in Fig. S2, likely due to factors including overlapping combination bands in this energy range, inadequate statistics, and mode dispersion.

A slight increase is apparent in the neutron energy loss values for the H rattling modes in the CeNiIn$_2$ octahedra compared to La$_3$NiIn$_2$ octahedra. The modes blue-shift slightly from 52.1(1) meV, 122.0(5) meV, and 158.6(5) meV in the La congener to 56.4(2) meV, 123.9(8) meV, and 158.7(3) meV in the Ce compound, respectively. These shifts may arise from a slightly stronger R–H interaction in the Ce compound at the 12I octahedral site stemming from a slightly larger Pauling electronegativity value for Ce (1.12) than for La (1.1) (H Pauling electronegativity = 2.2) [47].

3.2. Comparison to structurally and chemically similar CeNiSnH$_x$ hydrides

As a comparison to the RNiInH$_x$ compounds, we synthesized and studied the CeNiSnH$_x$ ($x = 1$–2) hydrides. Earlier, the CeNi tetrahedra in CeNiSnH$_x$ were hypothesized as the most likely hydrogen sites based on XRD measurements [48]. However, these sites in CeNiSnH$_x$ have never been crystallographically identified by neutron diffraction measurements. Here, we present PND measurements of CeNiSnH$_x$, CeNiSnH$_{1.43}$, and CeNiSnH$_{1.236}$ (mixed sample of the $x$=1 and $x$=2 compounds). The PND measurements of the CeNiSnH$_{1.43}$ sample indicate a mixture of CeNiSnH$_x$ with 53% of the monohydride, $x=0.97(1)$ and 47% of the dihydride, $x=1.94(2)$ (yielding an overall $x=1.43$). We find that these compounds crystallize in the Pna$_2$_1 ($x =$ 1) and the P6$_3$mmc ($x =$ 2) space groups, in agreement with the earlier diffraction measurements conducted on these metal hydrides (Figs. S6–S8) [34,49]. In the $x =$ 2 compound, the D atoms indeed occupy the CeNi interstitial sites, as suggested earlier based on the structure of the analogous LaNiSn$_2$ compound [48]. A significant difference in CeNiSnH$_x$ (Fig. S3b) compared to CeNiSnH$_{1.236}$ (Fig. S3c) is that every other Ni atom in the Ni–H–H–Ni–H–H–Ni chain is substituted with a Sn atom. The $R_3$-face-sharing of adjacent $R_3$Ni tetrahedra is replaced by $R_3$-face-sharing between adjacent CeNi and Ce$_2$Sn tetrahedra, forming NiCe$_2$Sn trigonal bipyramids. Deuterium (hydrogen) occupation of the Ce$_2$Sn tetrahedra is not observed in the structure, and chains of Ni–H–H–Ni–Sn–H–Ni run in the (001) crystallographic direction (where $\delta$ denotes the lack of an H atom, because the Sn atoms do not form chemical bonds in the (001) direction; Fig. 3b). Because the Ce$_2$Sn tetrahedra are not occupied by D atoms, the Switendick-Westlake criterion is not violated in the CeNiSnH$_x$ compounds.

The neutron vibrational spectra measured for CeNiSnH$_{1.43}$ and CeNiSnH$_x$ are shown in Fig. 4 together with the corresponding simulated phonon spectrum based on the DFT calculations. The neutron vibrational spectrum measured for CeNiSnH$_{1.43}$ is shown in Fig. 4 (top). The modes for CeNiSnH occur at neutron energy loss values of 102.01(3) meV ($\approx$ 839 cm$^{-1}$), $\approx$ 118.91(2) meV ($\approx$ 951 cm$^{-1}$), and 156.21(5) meV ($\approx$ 1255 cm$^{-1}$). Aided by animations of these modes generated from the DFT calculations, we assign these as bending, bending, and $\nu$(Ni–H) stretching modes, respectively. Similarly, for CeNiSnH$_x$, we identify modes at 85.93(4) meV ($\approx$ 693 cm$^{-1}$) and 140.63(4) meV ($\approx$ 1134 cm$^{-1}$), which we assign as $\delta$(H–Ni–H) bending and $\nu$(Ni–H) stretching modes, respectively. Four nearly degenerate stretching modes are calculated at $\approx$ 140 meV: two asymmetric stretching modes and two symmetric stretching modes differentiated by the in-phase or out-of-phase nature of the vibrations of the adjacent H–Ni–H moieties. These modes are calculated to occur at 130.1 meV (asymmetric, in-phase), 140.1 meV (symmetric, out-of-phase), 140.5 (asymmetric, out-of-phase), and 146.1 meV (symmetric, in-phase). Unlike the extensive energy dispersion across the Brillouin zone associated with the Ni–H stretching modes of the RNiInH$_x$ compounds, those for the CeNiSnH$_x$ compounds are rather sharp. This may be due to the H-metal alternating arrangement in CeNiSnH$_x$ resulting in a more harmonic and isolated local

Table 2

| Crystallographic parameters for CeNiSnH$_x$ (Pnma, a = 7.2804(5), b = 8.4838(5), c = 4.4064(3) Å, $V =$ 727.31(2) Å$^3$, CeNiSnH$_{1.43}$ (P6$_3$mmc, a = 4.3956(1), c = 5.8574(3) Å, $V =$ 143.020(5) Å$^3$), and CeNiSnH$_{1.236}$ (P6$_3$mmc, a = 4.3947(2), c = 5.8329(4) Å, $V =$ 142.72(1) Å$^3$). |
|-----------------|-----------------|-----------------|
| $a$ (Å) | $b$ (Å) | $c$ (Å) | $V$ (Å$^3$) |
| 7.2804(5) | 8.4838(5) | 4.4064(3) | 727.31(2) |
| 4.3956(1) | 5.8574(3) | 4.3947(2) | 5.8329(4) |
| 727.31(2) | 143.020(5) | 142.72(1) | 5.8329(4) |

Values in parentheses indicate ± 1σ.
environment around H, such that their vibrational behavior is better defined and more independent. In contrast, the two adjacent filled 4h sites in LaNiInH_{0.67} lead to complex H interactions with itself and its neighbors, thus the vibrational frequencies are more sensitive to the surrounding atoms, generating more dispersion. The spectral signatures for the close H–H contacts are absent in the CeNiSnH_{x} compounds, as expected based on the neutron diffraction-derived structures presented herein.

The modes corresponding to the dynamic motions of the hydrogen atoms in the Ce,Ni tetrahedra in CeNiSnH_{2} can be compared to the modes for the H atoms in the La,Ni tetrahedra in LaNiInH_{0.67}. The three modes in the measured spectral window for LaNiInH_{0.67} are the ν(Ni–H) stretching mode corresponding to the broad band from ≈ 80–106 meV and the two δ(H–Ni–H) narrowly split bending modes at 120.7(5) meV and 126.9(5) meV. In CeNiSnH_{2}, the bending and stretching modes occur at 85.93(4) meV and 140.63(4) meV, respectively. The bending mode is red-shifted by ≈ 40 meV while the stretching frequency is blue-shifted by ≈ 50 meV in the Ce compound compared to the La compound. These changes in energy may arise due to tighter confinement of the H atoms due to a smaller La_{3} face in the R_{3}Ni tetrahedra. The La–La distance is ≈ 4.05 Å compared to a Ce–Ce distance ≈ 4.40 Å, leading to the polyhedral volumes of ≈ 4.81 Å^{3} and ≈ 5.95 Å^{3}, respectively).

4. Conclusions

In conclusion, we report here for the first time the vibrational spectroscopic signature associated with H atoms with close H∙∙∙H contacts in violation of the Switendick-Westlake criterion in a metal hydride. We investigated the compounds RNiInH_{x} (R = La, x = 0.67, 1.6; R = Ce, x = 1.4), which contain close H∙∙∙H contacts in face-sharing R_{3}Ni tetrahedra above x = ⅔. We studied these compounds using NVS measurements coupled with DFT calculations. Assisted by the simulated spectra based on these calculations, we assign the observed spectral modes for these compounds. The two RNiInH_{x} metal hydrides studied here for R=La display two modes in the neutron vibrational spectra which arise from the basal plane H atom vibrations in the R_{3}Ni tetrahedra. As the loading increases above x = ⅔, the Switendick-Westlake criterion is violated, and these modes undergo significant softening and increased splitting because of the interaction of the close H atoms in neighboring R_{3}Ni tetrahedra (d(H–H) ≈ 1.6 Å). As a comparison, we also synthesized and studied the structurally similar CeNiSnH_{x} (x = 1.0, 2.0) compounds using PND and NVS measurements combined with DFT calculations. During the hydrogenation of the CeNiSn intermetallic alloy with a TiNiSi-type orthorhombic structure, two hydrides are formed, a monohydride CeNiSnH (orthorhombic, deformed TiNiSi type) and a dihydride CeNiSnH_{2} (hexagonal, filled ZrBeSi type). These compounds do not display the structural or spectroscopic signatures of close H–H contacts. We envision that the results presented herein will aid future characterization of metal hydrides using NVS measurements and may help guide the effort towards developing new metal hydride species with enhanced hydrogen storage capacities at operationally relevant temperatures.
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

R.A.K. acknowledges funding by the U.S. Department of Energy (USDOE), Office of Energy Efficiency and Renewable Energy (EERE), Hydrogen and Fuel Cell Technologies Office (HFTO) under contract no. DE-AC36-8GO28308 to the National Renewable Energy Laboratory (NREL). R.B.X. gratefully acknowledges research support from the Hydrogen Materials - Advanced Research Consortium (HyMARC), established as part of the Energy Materials Network under the USDOE EERE HFTO, under Contract Number DE-AC05-00OR22725. The computing resources for DFT and INS simulations were made available through the VirtuES and the ICE-MAN projects, funded by Laboratory Directed Research and Development program and Compute and Data Environment for Science (CADES) at ORNL. V.A.Y. and R.V.D. acknowledge a support from the EU Horizon 2020 program in the frame of the H2020-MSCA-RISE-2017 action HYDRIERE4MOBILITY project, with Grant Agreement 778307. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to license or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2021.162381.

References

[27] Al and Th-


