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Synthesis of Ni$_2$H$_3$ at high temperatures and pressures

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In situ high-pressure high-temperature synchrotron x-ray diffraction studies of the nickel-hydrogen system reveals the synthesis of a nickel polyhydride, Ni$_2$H$_3$. We observe the formation of NiH at pressures above 1 GPa, which remains stable to 52 GPa at room temperature. Laser heating to above 1000 K at this pressure initiates a transition to a phase which we determine as Ni$_3$H$_4$, crystallizing in a body-centered monoclinic unit cell. The Ni$_3$H$_4$ phase was observed to convert back to NiH below 25 GPa, and upon further decompression to atmospheric conditions, NiH slowly releases hydrogen with time.

The high-pressure synthesis and behavior of metal hydrides is an intensively studied topic of research due to the possibility of utilizing such materials for hydrogen storage purposes, and achieving predicted high-temperature superconducting states [1–3]. With the current consensus that reaching a metallic state of hydrogen remains outwith today’s capabilities of diamond-anvil cell (DAC) experiments, research interests have shifted to hydrogen-dominant metallic alloys, which have also been predicted to exhibit exotic properties, such as high-temperature superconductivity [4–9]. To date the formation of hydrogen-bearing species has been theoretically explored for the majority of elements in the periodic table and recently, polyhydrides of first-row transition metals have been synthesized at high pressures [10–12]. However, there remains a gulf between the number of systems explored at pressures above 50 GPa and the extensive predictions in the literature.

The nickel-metal-hydride system has been extensively studied due to its importance as an alternative to Li-ion batteries [14]. As such, the majority of studies at pressure have been generally limited to conditions achievable by industry. Nickel has long been known to form a primary solid solution (γ$_1$-NiH$_x$, with $x \approx 0.01$) near ambient conditions formed by the absorption of atomic H into the Ni lattice [15,16]. As pressure is increased above 1.25 GPa and $x$ approaches 1, Ni adopts a face-centered-cubic structure (γ$_2$-NiH) with $a = 3.731$ Å (an expansion of the pure Ni fcc structure with $a = 3.5238$ Å) with H atoms occupying the octahedral sites [15,17,18]. The effects of pressure and hydrogenation on the magnetism of NiH have recently been explored through both experimental and theoretical methods [2,19,20]. However, no predictions of nickel polyhydride species have been reported to date.

Here we report, through a combination of x-ray diffraction experiments and density functional theory (DFT) calculations, the synthesis and pressure-dependent behavior of a nickel polyhydride, Ni$_2$H$_3$. This compound can be synthesized at pressures exceeding 52 GPa, and is stable on decompression to 21 GPa, below which it decomposes to the known monohydride, γ$_2$-NiH. Quenching the sample to atmospheric conditions, we find that γ$_2$-NiH slowly releases molecular hydrogen over a period of 30 min as it decomposes to its constituent elements.

High-purity nickel powder (99.8%, 1.6 μm particle size) was loaded into DACs in an inert atmosphere, together with gold and/or ruby as a pressure marker and subsequently gas loaded with research-grade hydrogen gas (99.9999%) at 0.2 GPa [21,22]. Loading of hydrogen was confirmed by the observation of the hydrogen vibrational mode using a custom-built microfocused Raman system [6]. Rhenium gaskets were used to form the sample chamber in all experimental runs; diamond-anvil culets ranged from 200 to 300 μm, with sample sizes ranging between 50 and 125 μm once hydrogen was in the solid state. Angle-dispersive x-ray diffraction patterns were recorded on a fast image-plate detector with synchrotron radiation ($\lambda = 0.4131$ Å, 30 keV) at the BL10XU beamline, SPring-8, Japan [23]. Two-dimensional image-plate data were integrated with DIOPTAS to yield intensity vs 2θ plots [24]. Diffraction patterns were indexed with CONOGRAP; Le Bail and Rietveld refinement was carried out in JANA2006 [25–28]. Total energy calculations were carried out within the framework of DFT in conjunction with the projector-augmented wave method and a plane wave basis, as implemented in the VASP code [29,30]. We used the optB88vdw exchange-correlation functional [31,32] and included the Ni 3p, 4s, and 3d electrons in the valence space. Pure hydrogen phase I was modeled in an eight-molecule cell of $P6_3/m$ symmetry. The plane wave cutoff energy was 800 eV and Brillouin zone sampling was done on regular k-point grids with separations of 0.025 Å$^{-1}$.

After sample loading we observe the fcc structure of a primary solid solution γ$_1$-NiH$_x$, [$a = 3.5223(2)$ Å at 0.6 GPa]. On further compression above 1.0(5) GPa, the sample

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transforms to the stoichiometric $\gamma_2$-NiH phase indicated by the appearance of new diffraction peaks that could be indexed with an expanded fcc lattice, $a = 3.7329(1)$ Å. This observation is in good agreement with previous measurements [16,19,33]. Neutron diffraction has shown the H atoms to occupy the larger octahedral vacancies in this phase, in a similar fashion to CoH and other transition-metal hydrides [10,17,34,35]. In the absence of heating, this structure remains stable on compression to at least 52 GPa, which is in good agreement with theoretical predictions [20].

In situ laser heating under compressed hydrogen has been successful in synthesizing new transition-metal compounds, particularly polyhydrides of Fe, Cr, and Co [10–12,36,37] and was applied here to explore the possibility of synthesizing nickel polyhydride species. Samples of $\gamma_2$-NiH+H$_2$ were compressed to 34, 40, and 52 GPa and laser heated at each pressure. Following laser heating at 40 GPa new peaks could be observed in the diffraction pattern; however, these new unexplained peaks disappeared on returning to ambient temperatures. At 52 GPa, in situ x-ray diffraction patterns show the disappearance of peaks due to $\gamma_2$-NiH, which were replaced by numerous new peaks that remained on quenching (Fig. 1). Heating was localized to the NiH sample and temperatures were estimated to be less than 1000 K as no blackbody radiation was detectable from the sample during heating. All the observed peaks could be uniquely indexed to a body-centered monoclinic unit cell $a = 6.1137(3)$, $b = 2.4701(1)$, $c = 6.4019(3)$ Å, and $\beta = 93.603(4)^\circ$ at 52 GPa [38]. Systematic absences were consistent with space groups without glide-plane symmetry elements and structure solution by charge flipping suggested space group $I2/m$ [39]. Despite extensive texturing of the diffraction rings, Rietveld refinement could be applied to several datasets giving reasonable agreement factors in this space group. Ni-atom positions and thermal parameters could be refined, with two Ni-atom sites (see Fig. 1 caption for atomic positions).

Likely H-atom positions were identified using an electrostatic potential map based on DFT calculations of the Ni-atom unit cell. A range of possible stoichiometries were generated by the stepwise placement of H atoms, giving compositions from Ni$_2$H to Ni$_4$H$_2$. Evaluating the relative enthalpies shows only a single stoichiometry, Ni$_2$H$_3$, to become more stable than a combination of NiH and excess Ni or H$_2$: above 54.8 GPa Ni$_2$H$_3$ is more stable than 2 NiH + $\frac{1}{2}$H$_2$; by 60 GPa the formation enthalpy is $-11.6$ meV/Ni$_2$H$_3$. The optimized structure from DFT calculations is shown in Fig. 2; unit-cell dimensions and structural parameters are given in Table I. There are two unique Ni-atom positions coordinated by eight and seven H atoms, respectively, forming irregular polyhedra. Direct comparison of Ni-H bond distances between $\gamma_2$-NiH at the same pressure shows that the synthesis of Ni$_2$H$_3$ leads to an increase in coordination number without a significant

![Figure 1](image1.png)

**FIG. 1.** (a) High-pressure x-ray diffraction patterns ($\lambda = 0.4131$ Å) showing the synthesis of Ni$_2$H$_3$ by laser heating above 50 GPa. Tick marks indicate the positions of Bragg reflections from the noted phases. (b) Atomic volume as a function of pressure for Ni (black), $\gamma_2$-NiH (blue), and Ni$_2$H$_3$ (green). Fitted equations of state are shown with dashed lines; the equation of state of Ni is shown with a solid line [13]. Closed (open) symbols correspond to data collected on (de)compression. Inset shows raw image plates before and after laser heating showing the clear formation of textured rings due to Ni$_2$H$_3$. (c) Representative Rietveld refinement of Ni$_2$H$_3$ data at 52 GPa with Ni atoms at Ni1[0.7101(6), 0, 0.0640(6)] and Ni2[0.0671(5), 0, 0.2439(6)], $wR_p = 1.94\%$, $wR_{all} = 14.19\%$.

### Table I. Atomic position parameters refined by DFT for Ni$_2$H$_3$

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni1</td>
<td>4i</td>
<td>0.71014</td>
<td>0</td>
<td>0.06893</td>
</tr>
<tr>
<td>Ni2</td>
<td>4i</td>
<td>0.07325</td>
<td>0</td>
<td>0.24375</td>
</tr>
<tr>
<td>H1</td>
<td>2d</td>
<td>0</td>
<td>0</td>
<td>0.125</td>
</tr>
<tr>
<td>H2</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H3</td>
<td>4i</td>
<td>0.61809</td>
<td>0</td>
<td>0.30373</td>
</tr>
<tr>
<td>H4</td>
<td>4i</td>
<td>0.30209</td>
<td>0</td>
<td>0.38897</td>
</tr>
</tbody>
</table>
FIG. 2. (a) Ni$_2$H$_3$ unit-cell dimensions as a function of pressure. Inset: Crystal structure of Ni$_2$H$_3$ which crystallizes in space group $I2/m$ with two unique Ni atoms. (b) Ni$_2$H$_3$ unit-cell volume as a function of pressure. Inset: Ni$_2$H$_3$ structure showing four-coordinated H atoms in a distorted square planar arrangement. (c) Monoclinic angle, $\beta$, as a function of pressure. Data points in (a)–(c) are from experiments while lines correspond to values derived from DFT calculations at 0 K.

decrease in Ni-H bond distances. The structure of Ni$_2$H$_3$ partially retains the Ni$_4$H$_4$ cubic units of $\gamma_2$-NiH but in distorted form, additional H atoms (H2) are coordinated by four Ni atoms forming distorted squares in the $ac$ plane, breaking up the regular fcc lattice [inset, Fig. 2(b)]. The emergence of lower H-atom coordination has been predicted in several transition-metal hydrides and may lead to the formation of H-atom layers with increasing pressure and hydrogen content [11,40,41].

TABLE II. Birch-Murnaghan equation of state parameters for Ni [13], $\gamma_2$-NiH, and Ni$_2$H$_3$. $B'_0$ was freely refined for both NiH and Ni$_2$H$_3$.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$V_0$ ($\AA^3/Z$)</th>
<th>$B_0$ (GPa)</th>
<th>$B'_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni [13]</td>
<td>10.9315</td>
<td>181</td>
<td>5.2</td>
</tr>
<tr>
<td>$\gamma_2$-NiH (this work)</td>
<td>13.06(24)</td>
<td>191(10)</td>
<td>3.8(4)</td>
</tr>
<tr>
<td>$\gamma_2$-NiH [19]</td>
<td>13.14(2)</td>
<td>176(2)</td>
<td>4 (fixed)</td>
</tr>
<tr>
<td>Ni$_2$H$_3$</td>
<td>14.9(19)</td>
<td>204(43)</td>
<td>2.2(9)</td>
</tr>
</tbody>
</table>

$\gamma_2$-NiH to low pressures (0.34 GPa) at room temperature, and recovery to ambient pressure at low temperatures (85 K) have been observed before [43–45]. The metastable preservation to ambient pressure at room temperature is unexpected and the reason for this is not fully understood. The transition from $\gamma_1$-NiH + H$_2$ to $\gamma_2$-NiH is known to be sluggish so it is likely that the transition from $\gamma_2$-NiH to Ni + H$_2$ is also kinetically hindered which resulted in the continued presence of the $\gamma_2$-NiH structure at ambient pressure [45]. As the hydrogen content of the structure cannot be directly determined from our x-ray diffraction data, future large-volume neutron diffraction experiments exploring the synthesis and quench are imperative toward the consideration of $\gamma_2$-NiH as a hydrogen storage medium.

In conclusion, we have explored the Ni-H system up to pressures of 60 GPa with combined x-ray diffraction and laser heating. With this method we have synthesized a Ni$_2$H$_3$ species by reaction of $\gamma_2$-NiH and H$_2$ at pressures above 50 GPa. Ni$_2$H$_3$ remains stable down to approximately 17 GPa or if metal hydrides are inherently nonmagnetic. Note that recent structure predictions in a similar system, Cr-H, also exclusively find nonmagnetic hydrides [42]. Either way, this should not affect the stability of Ni$_2$H$_3$ against $\gamma_2$-NiH and H$_2$.

As can be seen in Fig. 3, on decompression below 25 GPa, weak peaks corresponding to $\gamma_2$-NiH begin to appear, and by 17.5 GPa, they fully replace those of Ni$_2$H$_3$. Reactions from $\gamma_2$-NiH could be observed down to ambient pressure and continue to remain upon opening the diamond-anvil cell to atmospheric conditions. Once quenched, we see the appearance of diffraction peaks corresponding to pure Ni and these reflections grow with time as the reflections from $\gamma_2$-NiH decrease in intensity. After approximately 1 h, no reflections due to $\gamma_2$-NiH could be observed leaving only those due to Ni (see Fig. 3).

The recovery of $\gamma_2$-NiH to low pressures (0.34 GPa) at room temperature, and recovery to ambient pressure at low temperatures (85 K) have been observed before [43–45]. The metastable preservation to ambient pressure at room temperature is unexpected and the reason for this is not fully understood. The transition from $\gamma_1$-NiH + H$_2$ to $\gamma_2$-NiH is known to be sluggish so it is likely that the transition from $\gamma_2$-NiH to Ni + H$_2$ is also kinetically hindered which resulted in the continued presence of the $\gamma_2$-NiH structure at ambient pressure [45]. As the hydrogen content of the structure cannot be directly determined from our x-ray diffraction data, future large-volume neutron diffraction experiments exploring the synthesis and quench are imperative toward the consideration of $\gamma_2$-NiH as a hydrogen storage medium.

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before transforming to $\gamma_2$-NiH. At ambient temperatures $\gamma_2$-NiH can be quenched to atmospheric pressure whereupon it releases $H_2$ as it slowly transforms into pure Ni.

*Note added.* Recently, an independent study described the prediction and subsequent experimental observation of the same Ni$_2$H$_3$ compound [46]. Their reported synthesis pressure (60 GPa) is higher than in this study (52 GPa); however, the decomposition pressure, unit-cell dimensions, and derived equation of state parameters are in close agreement with our data [46].

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[38] The standard C-centered cell can be obtained by application of the matrix $[(0, 0, 0), (0, 1, 0), (1, 0, 1)]$.