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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$_2$H$_3$, crystallizing in a body-centered monoclinic unit cell. The Ni$_2$H$_3$ phase was observed to convert back to NiH below 25 GPa, and upon further decompression to atmospheric conditions, NiH slowly releases hydrogen with time.

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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 ($\gamma_1$-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 ($\gamma_2$-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, $\gamma_2$-NiH. Quenching the sample to atmospheric conditions, we find that $\gamma_2$-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 CONOGRAPHE 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 $\gamma_1$-NiH$_x$ ($a = 3.5223(2)$ Å at 0.6 GPa]. On further compression above 1.0(5) GPa, the sample...
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 increase in bond length.

TABLE I. Atomic position parameters refined by DFT for Ni$_2$H$_3$ at 55 GPa, $a = 6.110$, $b = 2.467$, $c = 6.416$ Å, $\beta = 93.37^\circ$, space group $I2/m$.

<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>$\frac{1}{2}$</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 $I\overline{2}/m$ 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]. Over the stability range of Ni$_2$H$_3$ there is close agreement between the experimentally observed unit-cell dimensions and those derived from DFT calculations (Fig. 2), supporting our assignment of the hydrogen content. However, this should be experimentally verified by high-pressure neutron diffraction. The pressure-volume behaviors of NiH and Ni$_2$H$_3$ were fitted with third-order Birch-Murnaghan equations of state giving the parameters shown in Table II.

Magnetism was considered in the calculations for pure Ni, but not for the hydrides; a magnetic calculation of the $\gamma_2$-NiH rapidly demagnetized at all pressures. It is not clear whether this is an artifact of DFT preferring nonmagnetic solutions 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$_3$. Reflections 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.

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 synthetized 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

<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>
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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