INTRODUCTION

The finding of high temperature superconductivity in highly compressed H2S4 stimulated intensive research efforts into binary metal–H systems at high pressures, leading to the discovery of hydrogen-rich hydrides, also called superhydrides, under extreme pressure conditions.2-5 Hydrogen-rich hydrides display a wide variety of unforeseen and previously unimaginable hydrogen structures, ranging from clathrate-like cages (e.g., LaH10, CaH8)6-8 and oligomeric chain fragments (e.g., NaH6)9 to layer arrangements (e.g., FeH6).10 Characteristically, binary superhydrides are only stable at very high pressures in the Mbar range (70–150 GPa) and cannot be retained at ambient pressure. In contrast, ternary compounds may be retained and might even form under low(er) pressure conditions. Recently, it has been shown that already the application of modest pressures of around 5 GPa can afford new complex transition metal hydrides (CTMHs) in which group five and six metals attain unusually high coordination numbers in homoleptic complex ions such as [CrH5]6− and [NbH9]4−.11-13 Here, we demonstrate the accessibility of ternary hydrogen-rich hydrides in the Na–Ni–H system by using pressures up to 12 GPa and elevated temperatures up to 520 °C.

With the exception of Pd, late transition metals combine with elemental hydrogen only under high pressure conditions. The hydrogenation of Ni to γ-NiH requires about 1 GPa.14-16 A higher hydride, monoclinic Ni2H3, has been recently synthesized at 60 GPa.17 Both NiH and Ni2H3 cannot be quenched to ambient conditions. The situation changes radically when Ni is combined with an alkaline earth or rare earth metal. For example, the Ni-rich intermetallic compound LaNi5 absorbs readily hydrogen into interstitial positions with varying occupancies (LaNi5H6.5), and Mg2Ni is easily hydrogenated to yield the CTMH Mg2NiH4 featuring tetrahedral [NiH4]4− complexes.18,19 The nature of Ni–H interactions in...
the metallic interstitial hydride LaNi$_5$H$_{6.5}$ and the semiconducting CTMH Mg$_2$NiH$_4$ is rather different. There is even a third class of Ni hydride compounds, namely, perovskites (i.e., CaNiH$_2$)$_2$. Similar to CTMHs, Ni–H bonding in perovskites is covalent but delocalized over a polyatomic framework.

In contrast with its heavier congeners Pd and Pt, Ni does not appear to combine easily with alkali metals in ternary hydrides. There is only one known representative, recently reported LiNiH$_4$ with the perovskite structure, which has been obtained by high pressure synthesis at 3 GPa. Further, known hydrido complexes are restricted to tetrahedral [NiH$_4$]$^-$ with formally zero-valent Ni. Again, this is different to Pd and Pt, for which oxidation states of II (d$^8$) and even IV (d$^6$) are known in zero-valent Ni. $^{24}$ Again, this is different from the metallic interstitial hydride LaNi$_5$H$_{6.5}$ and the semiconducting CTMH Mg$_2$NiH$_4$ is rather different. There is even a third class of Ni hydride compounds, namely, perovskites (i.e., CaNiH$_2$)$_2$. Similar to CTMHs, Ni–H bonding in perovskites is covalent but delocalized over a polyatomic framework.

**EXPERIMENTAL METHODS**

**In Situ Powder X-ray Diffraction Studies at High Pressures.** The samples for the high pressure experiments were prepared in a glove box under an argon atmosphere because of air and moisture sensitivity of the starting materials. Powdered NaH (Sigma Aldrich, 90%) and powdered Ni metal (Sigma Aldrich, ≥99.9% trace metals basis) were carefully mixed at a molar ratio of 2:1 (NaH/Ni) and compressed into pellets. For the experiments at 5 and 10 GPa, sample pellets had an outer diameter (OD) of 2 mm and 1.5 mm height, while for the 12 GPa studies, dimensions were reduced to 1.4 and 0.75 mm, respectively. Ammonia borane (BH$_3$NH$_3$, Sigma-Aldrich, 97%) was used as hydrogen source. BH$_3$NH$_3$ has a well-defined decomposition behavior at high pressures and produces chemically inert BN as residual. $^{26,25}$ The amount of BH$_3$NH$_3$ used for each sample provided approx. 2.5 times molar excess of H$_2$ during the experiment with respect to nickel. NaH/Ni sample pellets were sandwiched between pelleted BH$_3$NH$_3$ and sealed inside NaCl capsules. The salt capsules employed at 5 and 10 GPa pressures had 3.0 mm OD and 3.8 mm height, while those used for 12 GPa runs were 2.4 mm OD and 2.8 mm height.

High pressure experiments at 5 and 10 GPa employed 14/8 multianvil assemblies. A detailed description of the 14/8 setup is provided elsewhere. $^{27}$ For reaching pressures above 12 GPa, the assembly was changed to a 10/5 type. Here, the sample capsules, protected by 2.8 mm OD BN sleeves, were inserted into 10 mm edge length Cr-doped MgO octahedra, along with two 2.8 mm OD ZrO$_2$ plugs and a nickel foil furnace (2.9 mm OD). Circular windows (2 mm OD) were cut in the Ni furnace along the beam direction to prevent the overlap with diffraction from the sample. Amorphous SiBCN rods (2 mm OD) and MgO rectangles (5 mm wide) were used as X-ray windows in the octahedra and gaskets, respectively, along the beam direction. Filled MgO octahedra were positioned between eight truncated tungsten carbide cubes (25 mm, Hawedia, ha7 grade) with 5 mm truncation edge length fitted with pyrophylite gaskets. Both 14/8 and 10/5 assemblies were compressed at a rate of 1 bar/min oil pressure (∼2.5 and ∼3.2 GPa/h, respectively) to the target pressures and heated in the Vöggenreiter-built modified-cubic press at beamline ID06-LVP, ESRF. $^{28}$ The heating was performed at various rates, ranging from 18 °C/min (comparatively fast) at T < 400 °C to <4 °C/min (comparatively slow) at higher temperatures or whenever a phase transition was expected. The heating was arrested each time the release of hydrogen from BH$_3$NH$_3$ was expected or the growth of ternary Na–Ni–H materials was detected. Pressure was estimated in situ from powder X-ray diffraction (PXRD) patterns using the equation of state (EOS) of NaCl, as reported by Birch. $^{29}$ For the 5 GPa experiments, temperature was evaluated from a D-type thermocouple calibration obtained in an independent run. The effect of pressure on the thermocouple EMF at 5 GPa is expected to be negligible. $^{30}$ During 10 and 12 GPa studies, the temperature was evaluated using the NaCl EOS. $^{29}$ Isobaric conditions were assumed during the heating, and the pressure was corrected after each ∼30 min dwell at constant power. Note that for the whole p, T range of the experiments, the Ni metal remained well below its melting curve. $^{31,32}$

Angle-dispersive PXRD patterns were collected continuously at a constant wavelength, selected by the Si (111) double-crystal monochromator from the emission of a U18 cryoundulator at ∼6 mm magnetic gap. For 5 and 10 GPa runs, the wavelength ($\lambda$) was 0.22542 Å (2.15–10.7° 2θ range) and for the 12 GPa experiment, $\lambda = 0.2296$ Å. At 12 GPa, data were collected in 1.66–10.18° and 2.86–11.34° 2θ intervals at different stages of the experiment. A Detection Technology X-Scan series 1 linear pixilated detector was used for data acquisition. A diffraction data set was typically saved every 32 s during compression and decompression and every 3.2 s during heating. This data set consists of 32 × 0.1 s sequential exposures, which were subsequently 32× rebinned. Sample-to-detector distance and detector offset were calibrated using La$_2$B$_6$Mg$_6$Ga$_6$O$_{24}$ (NIST). The in situ data were integrated, visualized, and manipulated using Fit2D software. $^{33}$ The 2θ angular positions of the diffraction peaks for the Na–Ni–H compounds and NaCl as a function of time were extracted from the compiled in situ data via the multiple fitting (MFIT) function in Fit2D. $^{34}$ Unit cell dimensions and volumes were extracted from the MFIT results by the least squares method. Indexing of powder patterns was done using the DICVOL algorithm within the CRYSFIRE package. $^{35}$

Products from the high pressure experiments were recovered in a glove box under an argon atmosphere. Approximately half of the product from each run was sealed inside a glass capillary for ex situ characterization by PXRD.

**Ex Situ PXRD Analysis.** PXRD patterns of recovered samples were collected at the beamlines ID15B and ID22 at the ESRF, Grenoble. The measurements at ID15B were performed at a constant wavelength of 0.41127 Å with the beam focused on a sample to 30 × 30 μm size and using a MarS55 flat-panel detector. The integration of 2D data was performed using Fit2D software. $^{36}$ High resolution synchrotron PXRD data were collected at ID22 using monochromatic radiation selected by a Si(111) crystal ($\lambda = 0.40008$ Å for the 5 GPa product and $\lambda = 0.3544$ Å for the 12 GPa product). Data acquisition was typically performed over a 0.5–32.9° 2θ range (0.002° step size) with the dedicated multianalyzer stage operating nine detectors in parallel, each preceded by a Si(111) analyzer crystal. $^{37}$

Le Bail analysis $^{37}$ and Rietveld refinement $^{38}$ of in situ and ex situ PXRD data were performed using Jana2006 software. $^{39}$ Before analyzing the patterns, they were corrected for background by subtracting the minimal value of observed intensity from the entire I$_{obs}$ column. For the data collected at ID22, the peak shape was fitted with a pure Lorentzian profile, while the rest of the refinements were performed using pseudo-

ACS Omega 2020, 5, 8710–8743
Voigt peak profile function. In addition, ID22 data were thinned prior to the refinement so that only every second data point was used. In situ PXRD data were prepared for refinements by averaging 10–30 datapoints collected during the temperature dwell, which improved the signal-to-noise ratio and decreased possible contributions of texture to the refinement.

EOS Calculations. The calculation of the EOS for the NaNiH$_3$ perovskite was based on the in situ PXRD data collected on decompression during the 12 GPa experiment. The pressures were estimated from the cell volumes of NaCl using EOS, as reported by Birch. The extracted data set of NaNiH$_3$ cell volumes as a function of pressure was introduced into EOSFit 5.2 software. Data quality did not justify the use of the third order BM EOS model, and second order Birch–Murnaghan (BM) EOS was used instead. In addition, EOSfit 5.2 was employed to extract the EOS from the density functional theory (DFT) calculated $p$, $V$ data. To make the resulting constants comparable with the fit of experimental data, a second order BM EOS model was used for the datasets obtained from DFT.

Theoretical Calculations. DFT enthalpy calculations were performed using the Vienna Ab Initio Simulation Package (VASP) in the framework of the projector augmented wave method within generalized gradient approximation and employing the Perdew–Burke–Ernzerhof parametrization of the exchange–correlation functional. The cutoff energy for the plane wave basis set was 500 eV for all simulations. Structural relaxations employed a $4 \times 4 \times 4$ Monkhorst–Pack (MP) $k$-point grid for $Pnma$ Na$_3$NiH$_5$ ($Z = 4$), a $4 \times 4 \times 4$ grid for $Cmcm$ Na$_3$NiH$_5$ ($Z = 4$) and Na$_3$NiH$_4$ (Na$_3$PtH$_4$ structure, $Z = 2$), a $14 \times 14 \times 14$ grid for the perovskites ANiH$_3$ ($A = Li, Na, K$), and $1 \times 1 \times 1$ ($\Gamma$-point) for $Z = 32$ Na$_3$NiH$_3$ supercells. Relaxations were performed with total energies converged better than $10^{-4}$ eV. Total energy calculations were carried out using the tetrahedron method with Blöchl correction on a $4 \times 4 \times 4$ MP $k$-point grid for $Pnma$ and $Cmcm$ Na$_3$NiH$_3$ and Na$_3$NiH$_4$ on a $14 \times 14 \times 14$ grid for the perovskites ANiH$_3$, and on a $2 \times 2 \times 2$ grid for $Z = 32$ Na$_3$NiH$_3$ supercells. For formation enthalpy calculations, total energy calculations were performed for NaH and Ni on 8 × 8 × 8 and 12 × 12 × 12 $k$-point grids, respectively. Molecular H$_2$ was considered with a pressure-independent enthalpy equal to −6.78 eV/molecule, as obtained from a total energy minimization of the H$_2$ molecule in a 10 × 10 × 10 Å$^3$ box.

Electronic density of states (DOS) calculations used spheres around the atomic sites (parameter RWIGS in VASP) with radii Na = 1.4, Ni = 0.8, and H = 1.1 Å. Bader analysis of the charge densities was performed according to refs and 51. The phonon dispersions and the phonon partial DOS were calculated on 2 × 2 × 2 supercells using the small displacement method as implemented in Phonopy. Total energies were converged better than $10^{-8}$ eV, referring to a $1 \times 1 \times 1$ Γ-only (Na$_3$NiH$_3$) and a $8 \times 8 \times 8$ k-point grid (NaNiH$_3$). The ionic positions were relaxed before the phonon calculations. The $T_c$ estimation was performed using the Quantum Espresso code and the Allen–Dynes-modified McMillan equation. The cutoff energy for the plane waves was set to 60 Ry. The self-consistent calculations were performed on a 32 × 32 × 32 $k$-point grid. The electron–phonon coupling calculation was performed on a 4 × 4 × 4 $k$-point grid and using 0.1 as the value for the Coulomb pseudopotential $\mu$.

Ab initio molecular dynamics (MD) simulations of cubic Na$_3$NiH$_4$ in the NVT ensemble (i.e., maintaining the number of atoms $N$, volume of the system $V$, and temperature $T$) were performed using the Nosé–Hoover thermostat at 1000 K and the experimental volume at ~5 GPa and 510 °C ($a = 7.19$ Å). The simulation was done on a 2 × 2 × 2 supercell ($Z = 32$, 288 atoms) of the cubic unit cell of the HT-HP Na$_3$NiH$_4$ phase. The Brillouin zone integration was done at the $\Gamma$-point.

RESULTS AND DISCUSSION

Formation of Na$_3$NiH$_3$ at 5 GPa and Its Recovery to Ambient Pressure. Throughout this study, reaction mixtures NaH/Ni/BH$_3$NH$_3$ 2:1:~0.8 were employed which corresponded to a Ni/H$_2$ ratio 1:~2.5. In total, three experiments were performed at pressures around 5 GPa. All experiments showed good reproducibility of observations. In the following, we describe an experiment, compiled in Figure 1, during which slow heating/cooling rates and prolonged annealing steps were applied, and diffraction data were acquired for structural analysis.

The sample was compressed to ~5.4 GPa and then heated to ~340 °C. At these $p$, $T$ conditions, BH$_3$NH$_3$ is expected to be completely decomposed into BN and hydrogen fluid. The sample was then kept at 340 °C for about 30 min in order to equilibrate the system in the presence of hydrogen fluid. Before the initial heating was finished, formation of $\gamma$-NiH (NiH$_x$) was noted at ~300 °C as a set of diffuse peaks that appeared near the Ni metal reflections at lower 2Θ angles. This is shown in the inset of Figure 1. In $\gamma$-NiH, the arrangement of metal atoms of face-centered cubic (fcc) Ni is retained, while H atoms are introduced in the octahedral voids of the metal structure, resulting in an expansion of the unit cell parameter. Upon further heating, at approx. 435 °C, a new set of reflections emerged in the PXRD patterns. The $d$-spacings of these reflections could not be matched to any known compound, and their presence was interpreted as formation...
of a ternary high pressure, high temperature phase, in the following denoted HT-HP Na$_3$NiH$_5$. These new diffraction lines became more pronounced, and their intensities increased further when dwelling at 510 °C for 80 min (Figure 1). The diffraction peaks from HT-HP Na$_3$NiH$_5$ were indexed to a fcc lattice, with $a \approx 7.19$ Å at 510 °C.

After the dwell, the sample was slowly cooled at a rate of $\sim 5$ °C/min. At about 330 °C, a new set of intense diffraction peaks replaced those of the HT-HP Na$_3$NiH$_5$ phase, indicating a transformation to a low temperature polymorph (LT-HP Na$_3$NiH$_5$). The transition completed almost instantly (within 60 s). The LT-HP phase was indexed to a C-centered orthorhombic lattice (extinction symbol C-c-) with the unit cell parameters $a \approx 7.34$ Å, $b \approx 6.88$ Å, and $c \approx 7.22$ Å at 320 °C. The sample was dwelled for about 20 min and then slowly (3.5 °C/min) heated again to check the reversibility of the observed phase transition. The back-transformation of LT-HP Na$_3$NiH$_5$ to the HT-HP phase occurred at $\sim 345$ °C. Again, the transition proceeded instantaneously. After the transformation, the sample was dwelled at $\sim 365$ °C for 10 min and then quenched to room temperature. The HT-HP phase was not preserved by rapid cooling but was replaced with LT-HP Na$_3$NiH$_5$. The pressure was estimated as $\sim 4.4$ GPa after the temperature quench.

Figure 2a shows the unit cell parameters of both phases as a function of temperature and time as extracted from the in situ PXRD data. In addition, changes in the cell volumes are shown in Figure 2b. The average standard deviations for the cell parameters and unit cell volumes are within $\pm 0.0052$ Å ($\pm 0.461$ Å$^3$) and $\pm 0.0013$ Å ($\pm 0.117$ Å$^3$) for the HT-HP and LT-HP phases, respectively. The close numerical range of their cell parameters and volumes suggests that the two phases are polymorphs and that the orthorhombic lattice results from a distortion of the HT cubic cell on cooling. The splitting of the 220 reflection of the cubic HT phase during the transition to orthorhombic is shown in Figure S1. The volume change at the cubic to orthorhombic transition is approx. $-2.1$ Å$^3$ (0.57%). The rapid character of the transformation and rather small temperature hysteresis are indicative of a first order displacive phase transition.

To conclude the experiment, the sample was decompressed to ambient conditions. At $\sim 2.9$ GPa, new diffraction peaks emerged. At $\sim 2.6$ GPa, the intensities of the new peaks increased, while the diffraction peaks of LT-HP Na$_3$NiH$_5$ became noticeably weaker, suggesting transformation to a different, low pressure, phase (LP Na$_3$NiH$_5$, see Supporting Information, Figure S2). At 1.4 GPa, the diffraction peaks of LT-HP Na$_3$NiH$_5$ were completely replaced. On final decompression, no significant further changes were observed, except for $\gamma$-NiH reverting back to fcc Ni. The sample was recovered at ambient conditions and used for ex situ PXRD examination. LP Na$_3$NiH$_5$ displayed a dark gray color, and when stored under Ar at room temperature, it decomposed over a period of several months.

**Elucidating the Composition and Crystal Structures of Polymorphic Na$_3$NiH$_5$.** For structural analysis of HT-HP and LT-HP Na$_3$NiH$_5$, PXRD data were prepared by averaging 20–40 patterns collected during the temperature dwell at 365 °C (cubic phase) as well as during the dwell at 320 °C and after the quench (orthorhombic phase). The HT-HP phase was analyzed using Le Bail fits to the space group Fm$ar{3}$m (225), whereas for the LT-HP phase space group Cmcm (63) was used. The $a$ parameter for the cubic phase at 365 °C was refined to $\approx 7.169$ Å. The cell parameters of the orthorhombic LT-HP phase at 320 °C were determined as $a \approx 7.344$ Å, $b \approx 6.883$ Å, and $c \approx 7.225$ Å. Possible metal atom arrangements were then identified using the Superflip algorithm on the extracted intensities within the Jana2006 package. For the HP-HT phase, an antifluorite arrangement of the metal atoms was suggested, with Ni and Na occupying 4$a$ and 8$c$ Wyckoff sites, respectively. However, this solution could not be fitted reasonably to the experimental data using Rietveld refinement (see Supporting Information for details). The fit improved significantly when an additional atom partially occupied the 4$b$ site, resulting in a Heusler arrangement of metal atoms. However, the type of atoms at this site was ambiguous: the Rietveld fit was equally good if 4$b$ was occupied by $\sim 0.3$ Ni or $\sim 0.7$ Na atoms, yielding metal atom compositions Na$_3$Ni$_{1.1}$ and Na$_{2.5}$Ni, respectively. An analogous result was obtained for the orthorhombic LT-HP phase (Cmcm): Na and Ni atoms were found to occupy 4$c$ and 8$e$ sites, respectively, with one more atom partially occupying a second 4$c$ site. The resulting compositions for the LT-HP phase reproduced those of the cubic polymorph. The simulated patterns for both cubic and orthorhombic phases with a metal atom composition Na$_3$Ni$_{1.1}$ are overlaid in the in situ PXRD data in Figure 1 (cf. Figure S2 in the Supporting Information).

Further structural investigations then targeted the product LP Na$_3$NiH$_5$ recovered at ambient conditions. The structure determination and refinement were performed using integrated

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**Figure 2.** Cell parameters (a) and volumes (b) of cubic HT-HP and orthorhombic LT-HP Na$_3$NiH$_5$ as a function of temperature at $\sim 5$ GPa. Errors corresponding to the symbol size or smaller are not shown.
2-dimensional PXRD data (cf. Supporting Information, Figure S3). Apart from leftover Ni metal and NaH, a set of reflections was present in the pattern, which could not be assigned to any known compound. The best indexing result suggested an orthorhombic unit cell with a Pn-a extinction symbol and approximate cell parameters $a \approx 10.41$ Å, $b \approx 7.37$ Å, and $c \approx 5.43$ Å. Le Bail analysis was initially carried out within the P222 (16) space group. A subsequent space group test then suggested Pnma (62). Structure solution resulted in a metal arrangement with 3Na:1Ni stoichiometry (Ni on a Wyckoff site 4c, and Na on sites 4c and 8d) and atomic coordinates very similar to K and N atoms in Pnma K$_3$NO$_4$ (potassium orthonitrate), see Supporting Information for details. The obtained structure was used for Rietveld refinement against the experimental data and fitted well to the observed diffraction pattern ($R_{\text{obs}} \approx 7.7\%$, see also Supporting Information for refinement procedure), which strongly indicated the correctness of the metal composition and metal atom arrangement in LP Na$_3$NiH$_5$. Consequently, the Na$_3$Ni stoichiometry was also assumed for the HP forms. A Na$_3$Ni metal composition suggested 5 H atoms and Ni in an oxidation state II (d$_8$) or less likely 4 and 3 H atoms with Ni in the oxidation state I (d$_9$) and octahedral voids. (b) Local coordination of a NiH$_5$ complex by 9 Na cations (top) and structure of a NiH$_5$ complex (bottom). Interatomic Na−Ni and Ni−H distances as obtained from DFT calculations are indicated (in angstroms).

The most stable Na$_3$NiH$_5$ configuration found by DFT optimization is shown in Figure 3, and its parameters are compiled in Table 1. The structure can be interpreted as a cubic close packing of NiH$_5^{3-}$ complexes with all tetrahedral and octahedral interstices filled by Na$^+$ ions (Figure 3a). The distribution of Ni atoms follows the fcc metric; however, the location of cations deviates substantially from the ideal centers of interstices (i.e., 4b and 8c in Fm3m). The local coordination and geometry of a NiH$_5^{3-}$ complex is shown in Figure 3b. In the NiH$_5^{3-}$ complex, the four basal ligands have similar and short distances to Ni (1.53 × 2, 1.55 × 2 Å), whereas the bond to the apical ligand is rather elongated (1.67 Å).

The optimized DFT structure of Pnma LP Na$_3$NiH$_5$ was then used as a model for a final Rietveld refinement against the experimental pattern. The hydrogen atom positions were kept unchanged during the refinement, and their $U_{\text{iso}}$ parameters were fixed at 0.038 Å$^2$ ($B_{\text{iso}} = 3$ Å$^2$). The refinement procedure is described in Supporting Information. The refinement details and obtained crystal structure parameters are included in Tables 3 and 4, and the final Rietveld fit is shown in Figure 4. A simulated PXRD pattern of Pnma LP Na$_3$NiH$_5$ is overlaid in the compilation of in situ PXRD patterns collected during decompression (Figure S2).

Following the results of the LP Na$_3$NiH$_5$ structure solution, the elucidation of the HT-HP and LT-HP structures was revisited using Na$_3$NiH$_5$ stoichiometry. For a more detailed analysis of the HT-HP phase, a 2 × 2 × 2 supercell ($Z = 32$) of the fcc Heusler arrangement of Na and Ni atoms was assembled and 5 H atoms were placed around each Ni atom. This was then used as the initial structure for NVT ab initio
MD simulations using the experimental volume at ~5 GPa and 510 °C (a = 7.19 Å). The simulation temperature was 1000 K. The system equilibrated after 1 ps, as indicated in the almost zero hydrostatic stress attained after this time (see Supporting Information, Figure S4), and NiH$_5^{−}$ complexes were found to perform reorientational dynamics (Figure S5). Accordingly, the fcc HT-HP Na$_3$NiH$_5$ structure can be considered as a time-averaged Heusler arrangement of Na ions and dynamically disordered NiH$_5^{−}$ complexes. This arrangement of metal atoms is shared with K$_3$ReH$_6$ which possesses ordered octahedral d$^4$ ReH$_6^{3−}$ complexes. Figure 5a displays an MD snapshot and the corresponding simulated fraction pattern. The kink in the $E−V$ curve between 10 and 10.5 Å$^3$ is attributed to an orientation change of complexes. The enthalpy difference between the HT-HP and LT-HP phases can be estimated as 10 meV/atom (8.6 kJ/mol). The equilibrium volume for both phases is near 11.1 Å$^3$/atom (note that both phases have also very similar volumes at the experimental conditions of the phase transition, cf. Figure 2), whereas the calculated equilibrium volume for Pnma LP Na$_3$NiH$_5$ is 11.6 Å$^3$/atom. Below 1.5 GPa the Pnma phase is more stable than the Cmcm one, which is in reasonable agreement with the decompression experiment where the phase transformation was observed in the range 2.5−3 GPa at room temperature.

Table 3. Results of the Rietveld Refinement of Na$_3$NiH$_5$ Polymorphs under Different p, T Conditions

| phase | LP Na$_3$NiH$_5$ | HT-HP Na$_3$NiH$_5$ | LT-HP Na$_3$NiH$_5$ | LT-HP Na$_3$NiH$_5$ |
|-------|------------------|---------------------|---------------------|---------------------|
| temperature | RT (300 K) | 365 °C (638 K) | ~5 GPa | ~5 GPa |
| pressure | ambient | | | ortorhombic |
| crystal system | orthorhombic | cubic | | ortorhombic |
| space group | Pnma (62) | Fm$ar{3}$m (225) | Cmcm (63) | Cmcm (63) |
| Z | 4 | 4 | 4 | 4 |
| lattice parameters (Å) | | | | |
| a = 10.4131(9) | a = 7.16905(16) | a = 7.3444(9) | a = 7.3575(13) |
| b = 7.3711(6) | | b = 6.8828(9) | b = 6.7932(15) |
| c = 5.4291(5) | | c = 7.2247(8) | c = 7.2231(12) |
| V (Å$^3$) | 416.71(6) | 368.456(15) | 365.218(8) | 361.0212(12) |
| V/Z (Å$^3$) | 104.18 | 92.114 | 91.303 | 90.255 |
| formula weight | 132.7 | 132.7 | 132.7 | 132.7 |
| $d_{m}$(g/cm$^3$) | 2.115 | 2.392 | 2.413 | 2.442 |
| $R_{int}$ (%) | 5.94 | 6.41 | 8.35 | 10.94 |
| $R_{f}$ (%) | 5.94 | 6.41 | 8.71 | 11.10 |
Parent Table 4. Fractional Coordinates and Atomic Displacement Parameters for the Various Na3NiH5 Polymorphs Obtained from Rietveld Refinement.

| atom     | site | x       | y       | z       | U_11 (Å²) |
|----------|------|---------|---------|---------|-----------|
| Ni (Ni+) | 4c   | 0.8812(7)| 0.25    | 0.7557(14)| 0.0191(17) |
| Na1 (Na+) | 8d  | 0.1528(12)| 0.0151(13)| 0.8209(18)| 0.025(3) |
| Na2 (Na+) | 4c  | 0.0731(13)| 0.25    | 0.372(3)  | 0.025(3)  |
|          |      |         |         |         |           |
|          | LT-HP Na3NiH5 (−5 GPa, 320 °C) |       |         |         |           |
| Ni       | 4c   | 0      | 0.2427(15) | 0.25    | 0.017(2)  |
| Na1      | 8e   | 0.210(3)| 0       | 0       | 0.070(6)  |
| Na2      | 4c   | 0      | 0.691(4)  | 0.25    | 0.070(6)  |
|          |      |         |         |         |           |
|          | LT-HP Na3NiH5 (−4.4 GPa, RT) |       |         |         |           |
| Ni       | 4c   | 0      | 0.2391(16)| 0.25    | 0.013(3)  |
| Na1      | 8e   | 0.208(2)| 0       | 0       | 0.046(6)  |
| Na2      | 4c   | 0      | 0.675(3)  | 0.25    | 0.046(6)  |
|          |      |         |         |         |           |
|          | HT-HP Na3NiH5 (−5 GPa, 365 °C) |       |         |         |           |
| Ni       | 4a   | 0      | 0       | 0       | 0.0118(19) |
| Na1      | 8e   | 0.25   | 0       | 0       | 0.054(3)  |
| Na2      | 4b   | 0.5    | 0.5     | 0.5     | 0.054(3)  |

*Hydrogen atoms for LP and LT-HP were introduced in the analysis from the DFT-optimized structures (Tables 1 and 2), and their positions were fixed during the refinement along with their ADPs [U_11 were set to 0.038 Å² (B_w = 3 Å²)]. H atoms for HT-HP were placed at a site 48h with x = 0.15 (Ni−H = 1.521 Å) and an occupancy of 5/12. See Supporting Information for Rietveld refinement procedures and resulting plots (Figures S6 and S7).

The investigation of the Na−Ni−H system was then extended to 10 GPa in order to further explore the polymorphic behavior of Na3NiH5 compounds and three libration (torsion) modes in the solid. Accordingly, the H-based modes in Na3NiH5 will distribute over three regions. Ni−H stretches are between 1300 and 1900 cm⁻¹. The two symmetric stretches (A_1) may be distinguished as apical (involving the apical H-ligand) and basal (involving the four basal H-ligands). The basal stretch is at the highest wavenumber (1830 cm⁻¹), whereas the apical one is at the lowest (1350 cm⁻¹). Six out of seven Ni−H bending/deformation modes are in the wavenumber range 600−800 cm⁻¹. One deformation mode attains a very low wavenumber (400 cm⁻¹) and falls in the spectral region of the libration modes (200−400 cm⁻¹).

Because of the sensitivity of Na3NiH5 toward decompression, we were not able to corroborate the vibrational modes suggested from the calculated phonon DOS by IR/Raman measurements. It is therefore instructive to compare with isoelectronic and isostructural CoH5⁻ and also NiH4⁻, for which vibrational properties have been reported earlier. For CoH5⁻ in Mg2CoH5, Co−H stretches are in a range 1632−1834 cm⁻¹. As in NiH4⁻, the two symmetric stretches represent the extremes. However, the basal stretch is at considerably higher wavenumbers compared to NiH4⁻. This is attributed to the large disparity of basal and apical Ni−H bond lengths. Bending modes for CoH5⁻ are between 766 and 1032 cm⁻¹ and thus higher than for NiH4⁻, which indicates that Co−H bonds are more rigid with respect to angular displacements. For NiH4⁻, stretching and bending modes are at lower wavenumbers compared to CoH5⁻ (1674−1691 and 620−791 cm⁻¹) and thus are more comparable to NiH4⁻. The liberation modes of Mg2CoH5 and Mg2NiH4 are at considerably higher wavenumbers (420−580 cm⁻¹) which is expected because the divalent, polarizing Mg²⁺ ions will create a more rigid torsional potential for the complex ions.

Formation of NaNiH₅ at p > 10 GPa and Its Recovery to Ambient Pressures. The investigation of the Na−Ni−H system was then extended to 10 GPa in order to further explore the polymorphic behavior of Na3NiH5 compounds and...
the possibility of forming other Na−Ni−H phases. The sample was heated at a starting pressure of 10.4 GPa at which initial H_2 release and complete decomposition of BH_3NH_3 are expected at 260 and 310−330 °C, respectively. The formation of γ-NiH became visible in PXRD patterns above 270 °C as a very diffuse peak near the 200 reflection of Ni (see upper part of Figure 9a). At 310 °C, the temperature was kept constant for about 35 min, after which heating was resumed at a slow rate (∼4 °C/min). Similar to the 5 GPa experiments, at about 440 °C, the growth of HT-HP Na_3NiH_5 was noted. However, at lower temperatures (350−380 °C), a set of very faint additional peaks was detected in the PXRD patterns (marked with red arrows in Figure 9a). The intensities of these new peaks continued to increase during further heating. To observe the development of the two phases, the sample was kept at ∼480 °C for ∼80 min. Intensities of the diffraction peaks for both HT-HP Na_3NiH_5 and the new phase noticeably increased during this time.

Figure 5. (a) Z = 32 MD snapshot of HT-HP Na_3NiH_5 at 1000 K (using the experimental volume at ~5 GPa and 510 °C) after equilibration (top) and calculated powder diffraction pattern (bottom). (b) DFT relaxed model of Cmcm LT-HP Na_3NiH_5 at 5 GPa (top) and calculated powder diffraction pattern (bottom). NiH_5^- complexes are drawn as green polyhedra.

Figure 6. Total energy vs volume and formation enthalpy versus pressure relations of HT-HP Na_3NiH_5, Cmcm LT-HP Na_3NiH_5, and Pnma LP Na_3NiH_5. Formation enthalpies refer to 3NaH + Ni + H_2.

Figure 7. Electronic DOS of Pnma LP Na_3NiH_5 at the equilibrium volume corresponding to ambient pressure (left) and schematic MO diagram for the 18 electron complex, showing the sequence of 5 Ni−H σ-bonding orbitals, 4 nonbonding, d-based, orbitals and the antibonding lowest unoccupied molecular orbital (LUMO) (right). The latter maps the crystal field splitting of the d orbitals. (Total DOS: black line, Ni-partial DOS: red line. Energy is plotted with respect to the Fermi level, E_F = 0 eV).

Figure 8. Phonon DOS (pDOS) of Pnma LP Na_3NiH_5 at the equilibrium volume corresponding to ambient pressure. pDOS is partitioned into atomic contributions of H, Na, and Ni.
The sample was further heated to 520 °C and then dwelled for 25 min. As a result, the reflections of the new phase became even more pronounced. To find out if the polymorphic behavior of the Na₃NiH₅ phase is preserved at ~10 GPa and to further observe the behavior of the new phase, the sample was cooled down to ~300 °C. The phase transition of HT-HP Na₃NiH₅ to the LT-HP polymorph occurred at ~320 °C, and upon reheating to 340 °C, the back-transformation was seen at ~335 °C. The temperature interval and rapid nature of the order–disorder transition closely mimicked the experiments at 5 GPa. During the course of these temperature variations, lasting for about 3 h, it appeared that the new phase grows slowly over time at the expense of the initially formed Na₃NiH₅ (cf. Figure S8, Supporting Information).

Afterward, the sample was heated to ~470 °C and subsequently temperature-quenched. As in the experiments at 5 GPa, the HT-HP phase underwent instant transformation to the orthorhombic LT-HP form on rapid cooling, whereas the diffraction peaks of the new phase remained unaltered. The pressure at room temperature was estimated as 8.9 GPa. The sample was then decompressed and recovered. PXRD characterization of the product revealed that the new compound was still present under ambient conditions, whereas LT-HP Na₃NiH₅ transformed to Pnma LP Na₃NiH₅ once again reproducing the behavior during the 5 GPa experiments.

The reflections of the new phase were indexed to a primitive cubic unit cell with no reflection conditions, and Pm₃m space group was used for further evaluation. The unit cell parameter 'a' varied within ~3.32–3.33 Å during the temperature variations of this experiment. Le Bail analysis and subsequent structure solution via Superflip resulted in a CsCl-type 1Na₁Ni metal arrangement. The cell parameter under ambient conditions was estimated as ≈3.43 Å, and the cubic perovskite structure NaNiH₃ was assumed for the new phase. This was confirmed by subsequent DFT calculations, which reproduced closely this cell parameter for the theoretical equilibrium structure. Consequently, it is inferred that at ~10 GPa, NaNiH₃ is initially formed for kinetic reasons and then superseded by the more thermodynamically stable NaNiH₃. To further investigate the effect of pressure on NaNiH₃ formation, an experiment at 12 GPa was conducted.

The compilation of PXRD patterns at ~12 GPa is shown in Figure 9b. The H release behavior of BH₃NH₃ at pressures above 10 GPa has not been explicitly determined. We estimate that complete decomposition at 12 GPa occurs around 350 °C. Growth of γ-NiH became apparent during ~15 min dwell at ~245 °C. During the same temperature dwell, extremely weak reflections of the NaNiH₃ phase appeared in the diffraction patterns. These peaks became increasingly prominent upon further heating. At ~335 °C, the diffraction peaks of HT-HP Na₃NiH₅ also started to emerge in the PXRD patterns. At this point, the temperature was dwelled for 20 min, and during the dwell the intensities of reflections for both HT-HP Na₃NiH₅ and NaNiH₃ continued to increase. Their cell parameters under these conditions were estimated as ≈6.89 and ≈3.30 Å, respectively. When the heating was resumed and the estimated temperature reached 400 °C, diffraction peaks of HT-HP Na₃NiH₅, NaNiH₃, and γ-NiH almost instantly disappeared, while at the same time, the intensities of NaNiH₃ increased remarkably (lower part of Figure 9b). After a 5 min dwell at 400 °C, the sample was cooled to room temperature. Noticeable changes occurred to the NaNiH₃ pattern, and no other NaNi–H phases could be detected. At room temperature, the estimated pressure was 10.6 GPa. The cell parameter of NaNiH₃ after cooling corresponded to ≈3.295 Å.

The in situ PXRD data collected on decompression were further used to extract the unit cell volume of NaNiH₃ as a function of pressure. Figure S9 (Supporting Information) shows the pressure–volume EOS of NaNiH₃. The bulk modulus extracted from the experimental data is 69.9(1) GPa. This is somewhat lower than the DFT calculated value [80.8(4) GPa] and may indicate the presence of H defects in NaNiH₃ that is, NaNiH₃−δ. H deficiency in transition metal perovskite hydrides is especially known for the Pd-based representatives CaPdH₃–δ and SrPdH₃–δ (δ ≈ 0.1).

After the decompression, the sample was recovered for ex situ characterization. The sample color appeared brown with an orange tint and slight metallic luster. A high-resolution PXRD pattern confirmed Pm₃m NaNiH₃ as the main product in the sample. The overall Rietveld fit is shown in Figure 10. A magnification of the high angle region and full width at half-maximum (FWHM) values for diffraction peaks as a function of pressure is plotted in Figure 11. The overall behavior of NaNiH₃ showed the expected phase changes when compared to the in situ PXRD patterns.
of 2θ, strongly corroborating a cubic metric for NaNiH₃, are shown as Supporting Information, Figures S10 and S11. Refinement details are given in Table 5 and as Supporting Information, Table S1. The lattice parameter at ambient pressure and room temperature is a = 3.43235(3) Å which implies a Ni–H distance of 1.716 Å.

| crystal system       | cubic          |  
|----------------------|---------------|
| space group          | Pm3m (221)    |
| Z                    | 1             |
| lattice parameters (Å) | a = 3.43235(3) |
| V (Å³)               | 40.4365(6)    |
| formula weight       | 84.7          |
| d_{200} (g/cm³)      | 3.478         |
| R_{Bragg} (%)        | 2.39          |
| R_{wp} (%)           | 2.39          |

Figure 10. Rietveld fit of the NaNiH₃ cubic perovskite structure to the ambient synchrotron PXRD data of the product after depressurization of the 12 GPa run (λ = 0.3544 Å). Excluded regions are shown in gray (see Supporting Information for refinement details). Inset depicts the cubic perovskite structure.

Figure 11 compares the (0 K) formation enthalpies of NaNiH₃ and NaNiH₄. Both systems are thermodynamically stable with respect to NaH + Ni + H₂, albeit weakly. The enthalpy change of the reactions NaH + Ni + H₂ → NaNiH₃ and 3NaH + Ni + H₂ → LP NaNiH₄ are estimated as ~0.43 eV/Z (~415 kJ/mol) and ~0.40 eV/Z (~386 kJ/mol), respectively, which is comparable to that of LaNi₄ hydrogenation (~32 kJ/mol H₂), ⁷¹ that is, high pressures are actually not required to stabilize these compounds. The significance of pressure for the synthesis of NaNiH₃ and NaNiH₄ is however two-fold. First, with pressure, the decomposition temperature will shift to higher values, thus enabling the application of elevated temperature for synthesis (>430 °C at ~5 GPa and reduced to ~300 °C at ~12 GPa). Second, kinetic barriers—present at ambient pressure—will be substantially reduced with increasing pressure. Importantly, the pressure dependence of the activity of molecular hydrogen is not well known (and thus not considered in our calculations). However, at pressures above 1 GPa, the activity of molecular hydrogen increases sharply, ⁷²,⁷³ which generally favors hydride formation.

The calculated formation enthalpies also suggest that the formation of NaNiH₄ is kinetically driven. The decomposition according to NaNiH₃ → NaNiH₂ + 2NaH is favored at ambient pressure and becomes increasingly favorable with increasing pressure. Computed decomposition enthalpies as a function of pressure are shown in Figure S12 (Supporting Information). In Figure 11, we also included the formation enthalpy for hypothetical NaNiH₄ with the Na₃PtH₄ structure and square planar d⁸-NiH₄²⁻ complexes. ⁷⁴ At ambient pressure, NaNiH₄ appears similarly stable as NaNiH₃ but becomes rapidly disfavored with increasing pressure.

Transition metal perovskite hydrides are elusive. Including NaNiH₃ from this work, there are 10 known representatives. Most correspond to combinations of Ni and Pd with the divalent cations Ca, Sr, and Eu. ⁷⁵ Lately, representatives with Co and Rh have been reported. ⁷⁶,⁷⁷ The electronic structure of transition metal perovskite hydrides has been analyzed earlier. ²¹,⁷⁶,⁷⁷ Figure 12a depicts the band structure of NaNiH₃ at the computed equilibrium volume. Spin-polarized calculations revealed a nonmagnetic ground state. Occupied bands are divided into bonding α₁g and eₗ nonbonding t₂g and antibonding eₗ*. The weakly dispersed t₂g band is completely filled for 12 e/Z. Accordingly, in NaNiH₃ with 14 e/Z, the eₗ*
stretches and 6 are Ni stretching modes, however, are in a similar range, 600–800 cm\(^{-1}\). The H stretching modes are considerably smaller in the Na\(H\) system for which the perovskite

electronic structure of LiNiH\(_4\) is very similar to NaNiH\(_3\) (cf. refs 76 and 77), phonon dispersions are rather different. In particular, the loose Li–H coordination is revealed in the Ni–H bonds which are at considerably lower wavenumbers compared to NaNiH\(_3\) (by 150 cm\(^{-1}\) as compared to 1.39 Å for Na\(^+\))\(^{78}\) would also be located within the stability field. Again, the result is included in Figure 11. KNiH\(_3\) has a positive formation energy for all pressures and is thus not expected to be thermodynamically stable. Note that KNiH\(_3\) has a negative formation energy with respect to the elements, K + Ni + 3/2H\(_2\).\(^{77}\)

Because transition metal perovskite hydrides are expected to be stable only as 14 and 15 e/\(Z\) systems,\(^{61,72,76}\) an interplay between complex hydride and perovskite formation will be expected. For Na–Ni–H, the CTMH Na\(_3\)NiH\(_5\) forms initially but is unstable toward decomposition to the perovskite according to 2NaH + NaNiH\(_3\). In both forms of hydrides, Ni is loosely coordinated in the cuboctahedral cavity of the perovskite structure. Whereas the electronic structure of LiNiH\(_4\) is similar to NaNiH\(_3\) (cf. refs 76 and 77), phonon dispersions are rather different. In particular, the loose Li–H coordination is revealed in the Ni–H bonds which are at considerably lower wavenumbers compared to NaNiH\(_3\) (by 150 cm\(^{-1}\) as compared to 1.39 Å for Na\(^+\))\(^{78}\) would also be

Table 6. Compilation of Bader Charges and Volumes (Å\(^3\))

| compound    | Na charge | Na volume | Ni charge | Ni volume | H charge | H volume |
|-------------|-----------|-----------|-----------|-----------|----------|----------|
| NaH         | 0.848     | 9.928     | –0.848    | 17.824    |
| NaNiH\(_3\) | 0.838     | 7.503     | 0.366     | 12.531    | –0.401   | 6.374    |
| Na\(_2\)NiH\(_3\) | 0.841     | 9.622     | 0.323     | 19.633    | –0.502   | 11.78    |
| Na\(_3\)NiH\(_5\) | 0.824     | 9.947     | 0.224     | 15.190    | –0.539   | 11.95    |

charge, >0.8, irrespective of the system, which corroborates its cationic, Na\(^+\), character in all systems. Na–H distances are at 2.43 and 2.45 Å for NaNiH\(_3\) and NaH, respectively, and in a range 2.45–2.81 Å for LP Na\(_2\)NiH\(_5\). Compared to NaH, constituting hydric H\(^+\), Bader charges and volumes for H are considerably smaller in the Na–Ni–H materials with covalent Ni–H bonding. Yet, the state of covalent bonding, localized and delocalized (metallic), can be discriminated. The perovskite is distinguished by small volumes of all constituting atoms, manifesting its compact structure.

Figure 12b depicts the phonon dispersions of NaNiH\(_3\) at the computationally relaxed equilibrium volume. The 5 atoms in the unit cell give rise to 12 optic modes, of which 3 are Ni–H stretches and 6 are Ni–H bends and the remaining 3 correspond to Na translations. The H stretching modes are around 1300 cm\(^{-1}\), which is considerably lower than the Ni–H stretches in LP Na\(_2\)NiH\(_5\) (1350–1850 cm\(^{-1}\)) because of the larger Ni–H bond length in the perovskite (cf. Figure 8). The bending modes, however, are in a similar range, 600–800 cm\(^{-1}\). Computation of the Eliashberg function and electron–phonon coupling integral show that electron–phonon coupling is negligible in NaNiH\(_3\), and thus, superconductivity is not expected.

With respect to NaNiH\(_3\), the formation of more stable NaNiH\(_3\) is kinetically hindered. Here, it is important to compare with the Li–Ni–H system for which the perovskite LiNiH\(_4\) was recently reported.\(^{23,76}\) Similar to NaNiH\(_3\), LiNiH\(_3\) was obtained from the reaction of LiH and Ni at high pressures in the presence of H\(_2\) fluid. However, this reaction already occurred at pressures around 3 GPa via an intermediate Li\(_x\)Ni\(_{1−x}\)H solid solution (based on γ-NiH\(_2\)). There was no evidence for complex hydride formation in the Li–Ni–H system. Possibly, CTHM formation is suppressed because Li\(_x\)Ni\(_{1−x}\)H enables a more favorable kinetics for LiNiH\(_3\) formation.

As included in Figure 11, the formation enthalpy of LiNiH\(_3\) is very similar to NaNiH\(_3\) at ambient and slightly elevated pressures, but LiNiH\(_3\) is destabilized considerably with respect to NaNiH\(_3\) with increasing pressure. Because of the small size of Li, the equilibrium lattice parameter of LiNiH\(_3\) is very small, 3.266(1) Å (cf. ≈3.432 Å for NaNiH\(_3\)). Accordingly, the Ni–H distance within the octahedral framework is reduced to ≈1.633 Å, which is comparable to the apical Ni–H distance in NaNiH\(_3\). A further decrease of the Ni–H distance by external pressure will then destabilize LiNiH\(_3\) with respect to NaNiH\(_3\).

Despite the small Ni–H distance in LiNiH\(_3\), Li\(^+\) remains loosely coordinated in the cuboctahedral cavity of the perovskite structure. Whereas the electronic structure of LiNiH\(_4\) is very similar to NaNiH\(_3\) (cf. refs 76 and 77), phonon dispersions are rather different. In particular, the loose Li–H coordination is revealed in the Ni–H bonds which are at considerably lower wavenumbers compared to NaNiH\(_3\) (by 150 cm\(^{-1}\) as compared to 1.39 Å for Na\(^+\))\(^{78}\) would also be located within the stability field. Again, the result is included in Figure 11. KNiH\(_3\) has a positive formation energy for all pressures and is thus not expected to be thermodynamically stable. Note that KNiH\(_3\) has a negative formation energy with respect to the elements, K + Ni + 3/2H\(_2\).\(^{77}\)

Because transition metal perovskite hydrides are expected to be stable only as 14 and 15 e/\(Z\) systems,\(^{61,72,76}\) an interplay between complex hydride and perovskite formation will be limited to hydrides of transition metals from groups 9 and 10. For Na–Ni–H, the CTMH Na\(_3\)NiH\(_5\) forms initially but is unstable toward decomposition to the perovskite according to NaNiH\(_3\) → 2NaH + NaNiH\(_3\). In both forms of hydrides, Ni is present in the oxidation state II. A related interplay example has been reported for Ca–Rh–H. Here, Ca\(_2\)Rh\(_{2x+y}\) is obtained from sintering mixtures of CaH\(_2\) and Rh at temperatures between 250 and 500 °C in a slightly pressurized hydrogen atmosphere (several bars).\(^{79,80}\) Mixed-valent Ca\(_2\)Rh\(_{2,5x+y}\) (x ≈ 0.4) crystallizes with a hydrogen-disordered K\(_2\)Pt\(_4\) structure, featuring locally isolated octahedral Rh(II)–H\(_{4x}\) and square pyramidal Rh(I)H\(_{4,5x}\) complexes. Furthermore, this synthesis strategy afforded also the more Rh-rich phases Ca\(_8\)Rh\(_{12,5z}\) and Ca\(_8\)Rh\(_{12,5z}\) in which additional Rh atoms are inserted in the K\(_2\)Pt\(_4\) structure and link previously

Figure 12. Electronic DOS (a) and phonon dispersion (b) for NaNiH\(_3\) at zero pressure.
isolated complexes through common H ligands. It has been conjectured that these more Rh-rich phases represent intermediates toward the perovskite CaRhH₃ according to Ca₂Rh(II)H₆ + Rh → 2 CaRh(I)H₇. The synthesis of CaRhH₃ has not yet been achieved from reaction mixtures CaH₂ + Rh + H₂, and we suspect that, similar to NaNiH₃, its formation via Ca₂Rh₁⁺H₆→CTMHs is kinetically hindered but should be possible when using high pressures. Recently, the Kohlmann group reported the synthesis of CaRhH₃ from a different route, CaRh₂ + H₂ → CaRhH₃ + Rh, using the Laves phase CaRh₂ as a precursor. This hydrogenation reaction proceeds under comparatively mild conditions, ~250 °C and 50 bar H₂ pressure.

Metallurgical transition metal hydride perovskites have been investigated for superconductivity early on. Orgaz et al. performed a computational study on the electron–phonon coupling in the Pd hydrides MPdH₃ (M = Ca, Sr, Eu, and Yb) but found only moderate to weak coupling, suggesting low values of the superconducting transition temperature. Indeed, Ayukawa et al. did not observe superconductivity for CaPdH₃ above 2 K. The superconducting properties of Ni hydride perovskites and CaRhH₃ are not known. Our calculations, however, indicate only a very weak electron–phonon coupling in NaNiH₃, and thus, superconductivity above 2 K is not expected.

## CONCLUSIONS

The application of high pressures afforded for the first time ternary compound in the Na⁻Ni–H system. Polymeric Na₃NiH₅ featuring square pyramidal complex ions NiH₅⁻⁻ was obtained from reaction mixtures NaH⁻Ni–H₅ at pressures between 5 and 10 GPa. NiH₅⁻⁻ represents the first homoleptic hydrido complex in which Ni possesses an oxidation state larger than 0 and binds to more than four ligands. At pressures above ~335 °C, Na₃NiH₅ adopts a fcc structure in which NiH₅⁻⁻ complexes are dynamically disordered (HT-HP Na₃NiH₅); at lower temperatures, the structure distorts orthorhombically and complexes appear ordered (LT-HP Na₃NiH₅). Upon pressure release, LT-HP Na₃NiH₅ undergoes a phase transition to a low pressure form (LP Na₃NiH₅) which can be recovered at ambient p, T. Na₃NiH₅ is unstable with respect to decomposition into the perovskite NaNiH₅ according to Na₃NiH₅ → NaNiH₅ + 2NaH, and it is inferred that its formation is kinetically driven. NaNiH₅, in which Ni is octahedrally coordinated by six H atoms, was obtained at pressures 10–12 GPa. Also, this ternary hydride phase can be recovered at ambient conditions. It is conjectured that with pressure, a similar interplay between complex hydride and perovskite phases can be observed in the CaH₂–Rh–H₅ system. Na₃NiH₅ and NaNiH₅ are further examples of ternary hydrogen-rich hydrides that form under comparatively low pressure conditions and can be retained at ambient pressure.

## ASSOCIATED CONTENT

1. Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00239.

Splitting of 220 reflection during the transition of HT-HP Na₃NiH₅ to LT-HP polymorph, formation of LP Na₃NiH₅ polymorph upon decompression of the 5 GPa run at RT, fragment of a 2D-PXRD pattern of the recovered LP Na₃NiH₅ product, deviatoric stress as a function of the simulation time for HT-HP Na₃NiH₅, probability map of angular positions of H atoms in NiH₅⁻⁻ complexes in the HT-HP and LT-HP phases, results of the Rietveld fit of the cubic HT-HP Na₃NiH₅ and the Cmcm LT-HP Na₃NiH₅ models to in situ PXRD data, results of the Rietveld fit of the Cmcm LT-HP Na₃NiH₅ model, changes in phase fractions of Na–Ni–H–products and nickel hydride during 10 GPa run, experimental and computed EOS for NaNiH₃, magnified high angle region of the NaNiH₃ perovskite structure Rietveld fit, FWHM values for NaNiH₃, diffraction peaks as a function of 2θ at ambient p, T, DFT-computed decomposition enthalpies for Na₃NiH₅ and NaNiH₅, comparison of the electronic band structure and phonon dispersions for NaNiH₃ and LiNiH₅, fractional coordinates and atomic displacement parameters obtained for the perovskite NaNiH₃, and details of the structure solution of the “Na₃Ni” arrangement for LP Na₃NiH₅ and the Rietveld refinement procedure for Na–Ni–H products. Crystallographic data of LP Na₃NiH₅ at ambient p, T (CIF)

Crystallographic data of HT-HP Na₃NiH₅ at 638 K and ~5 GPa (CIF)

Crystallographic data of LT-HP Na₃NiH₅ at 593 K and ~5 GPa (CIF)

Crystallographic data of LT-HP Na₃NiH₅ at RT and ~4.4 GPa (CIF)

Crystallographic data of perovskite NaNiH₅ at ambient p, T (CIF)

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**Notes**

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