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Synthesis of New Nickel Hydride at High Pressures.

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Abstract:

We predict two new nickel hydrides Ni_2H_3 (C2/m) and NiH_2 (I4/mmm) to be thermodynamically stable at 60 GPa by DFT calculations. The calculated structure of NiH_2 is similar to the one observed earlier for FeH_2 . However, to the best of our knowledge, the monoclinic structure predicted for Ni_2H_3 was never reported in the other hydrides. We successfully synthesized the monoclinic Ni_2H_3 phase using laser heating technique in a diamond anvil cell at pressures around 60 GPa. The Ni_2H_3 phase can be retained down to 17 GPa, and DFT calculations predict it to be nonmagnetic and non-superconducting. However, we did not find in our experiments the theoretically predicted NiH_2 phase. Higher pressures and/or different synthesis conditions might be needed to synthesize this and other polyhydrides of nickel. Our results show that Ni-H system behaves differently in comparison to the Fe-H system: Ni extends its own chemical identity to pressures as high as 60-80 GPa. This finding may have significant implications for the high-pressure behavior of Fe-Ni alloys at the high pressure conditions relevant for the Earth and planetary sciences.

The compressed hydrogen or hydrogen-rich materials are predicted to be high- T_c or even room-temperature superconductors due to the strong coupling of the conduction electrons to the high-frequency phonons as suggested by a number of theoretical calculations based on the BCS phonon-mediated theory [1]. However, these theoretical predictions were not experimentally proven until the discovery of superconductivity with superconducting T_c up to 200 K in a compressed H_2S [2,3], in agreement with previous theoretical work [4,5]. Currently, this discovery motivates scientists to look for high T_c superconductors in hydrogen-rich materials. As follows from many theoretical calculations, higher hydrogen content would usually lead to higher superconducting transition temperatures. Although many hydrides were predicted to exist based on theoretical calculations, very few of the predicted phases were confirmed by the experiments until now [6-8]. It is of significant interest to synthesize other hydrogen-rich materials to confirm or disprove the theoretically predicted new phases of these fascinating compounds.

A number of transition metal hydrides MH_x with $x>1$ have been synthesized until now, such as FeH_5 [8], IrH_3 [9], FeH_2 [10], FeH_3 [10], CoH_2 [11], $\text{MoH}_{1.4}$ [12], TaH_2 [13], RhH_2 [14], TiH_2 , ZrH_2 , HfH_2 , VH_2 , NbH_2 [15]. Because hydrogen is considered as a possible light element in the Earth's core, which is mostly composed of iron, iron hydrides have been studied in detail. In

particular, polyhydrides FeH_2 with $I4/mmm$, FeH_3 with $Pm\bar{3}m$ and FeH_5 with $I4/mmm$ can be synthesized under pressure at 67 GPa, 87 GPa and 130 GPa [8,10], respectively. Another important light transition metal element, nickel, is also one of the important elements in the Earth's core. However, the monohydride NiH phase is the only currently known compound of nickel and hydrogen at high pressure. By using a diamond anvil cell (DAC) combined with laser heating capabilities, very high pressures and temperatures can be achieved, which is crucial for the synthesis of the polyhydride phases of metals. Using laser heating in a DAC, we synthesized successfully a new nickel hydride Ni_2H_3 phase at high pressures guided by the theoretical structural search (the details of the theoretical calculations are provided below).

Method

A 20 μm -size Ni foil with thickness around 4 μm along with small fragments of Au was loaded with hydrogen in a diamond anvil cell (DAC) with 200 μm culet size [6]. Rhenium was used as gasket material. The XRD measurements and double-sided laser-heating were performed at Sector 13 (GSECARS) of the Advanced Photon Source at the Argonne National Laboratory. The sample was heated by a YAG laser at different pressures. More details on the laser heating system at GSECARS can be found in Ref. [16]. The DAC was cooled to 200 K with a nitrogen jet from a Cryostream-type unit manufactured by Oxford Cryosystems. Pressure was determined by the equation of state of gold (Au) [17]. A Pilatus 1M CdTe detector was used to collect angle-dispersive x-ray diffraction with a wavelength of $\lambda=0.3344$ Å. The heating spot was kept away from the gold and was aligned to avoid the sample parts touching the diamond anvil, in order to prevent the contamination by gold and carbon. The two-dimensional images were integrated into intensity versus (2θ) data using the DIOPTAS software [18]. GSAS was used to refine the data using the Le Bail method [19].

Our structural predictions approach is based on a global minimization of free energy surfaces merging ab initio total-energy calculations through CALYPSO (Crystal structure AnaLYsis by Particle Swarm Optimization) methodology as implemented in CALYPSO code [20,21]. The effectiveness of our CALYPSO method has been demonstrated by successful applications to predicting high-pressure structures of various systems, ranging from elements to binary and ternary compounds [21-24]. Structure searches were performed at 60 GPa using models consisting of 1-4 formula units. Local optimizations performed during structure search were done with the use of the conjugate gradients method and were stopped when the enthalpy changes became smaller than 1×10^{-5} eV per cell. The 60% of the lowest-enthalpy structures of each generation were used to produce the structures in the next generation by the local Particle Swarm Optimization technique, and the remaining structures (40%) were randomly generated within symmetry constraints to enhance the structural diversity. The inertia weight is dynamically varied and decreases linearly from 0.9 to 0.4. We keep the self-confidence factor and the swarm confidence factor constant and equal to 2. The magnitudes of the velocities are confined within the range of $[-0.2, 0.2]$. Typically, the structure searching simulation for each calculation was stopped after we generated 1000-1200 structures (e.g. about 20-30 generations). Each generation contained 40 structures, and the first generation was produced randomly within symmetry constraints. The structural relaxations were performed using density functional theory (DFT) within the Perdew–Burke–Ernzerhof (PBE) [25] parametrization of the generalized gradient approximation (GGA), as implemented in the Vienna ab initio simulation package (VASP) code [26]. The all-electron projector augmented wave (PAW) potentials [27] were used in these

simulations. The dense Monkhorst–Pack k-meshes [28] were used to ensure that the enthalpy calculations convergence was very good. The phonon calculations were carried out by using supercell approach as implemented in the “Phonopy” code. The Ni_2H_3 is demonstrated to be dynamically stable around 80 GPa by full phonon dispersion calculations. We did not include the zero-point energy in the calculations.

Results

In order to synthesize new nickel hydrides at high pressure, we began with structure searches at 60 GPa for NiH_x and found that the most stable phase is a cubic structure observed in previous experiments, confirming the validity of this computational scheme. Then we examined the thermodynamic stability of the Ni-H system using the enthalpies of formation relative to Ni and H at 60 GPa. At 0 K, the ground-state enthalpy of formation ΔH_f is defined as $\Delta H_f(\text{Ni}_x\text{H}_y) = G(\text{Ni}_x\text{H}_y) - (xG(\text{Ni}) + yG(\text{H})) / (x + y)$, where $G = E + PV$ and G , E , P , and V are enthalpy, total electronic energy, pressure, and volume, respectively. The ΔH_f for convex hull diagram was calculated for every stoichiometry at 60 GPa, using the lowest-enthalpy structure obtained from the structure searches. Here a negative ΔH_f indicates that the compound is more thermodynamically stable than the mixture of components, while the convex hull of ΔH_f connects all stable structures. The fcc structure of Ni and hexagonal close packed structure of H_2 were used as reference structures. We found that the Ni_2H_3 and NiH_2 are also stable at 60 GPa as shown in the convex hull calculations (Figure 1(a)). However, we do not find any stable NiH_3 and NiH_4 phases. Here, the Ni_2H_3 adopts a $C2/m$ space group with 4 formula units (f.u.) in the primitive cell at 60 GPa. The NiH_2 phase adopts a $I4/mmm$ space group with 4 f.u. in the primitive cell at 60 GPa. Fig. 1(b), (c) and (d) shows the structures of the predicted nickel hydrides. The NiH_2 structure is similar to the one reported earlier for FeH_2 [10], and it is isostructural with the theoretically predicted structure of CoH_2 [24]. However, the monoclinic structure of Ni_2H_3 has never been reported earlier for hydrides.

In order to synthesize the predicted new nickel hydrides, we used in-situ laser heating in a DAC. The metal piece of nickel reacts with hydrogen at low pressure and ambient temperature to form the fcc phase of NiH. We increased the pressure to 61 GPa around 200 K. The temperature was determined by the thermocouple attached to the diamond anvil. The fcc NiH structure remained intact indicating that no further reactions took place with hydrogen at low temperatures. The equation of state of NiH was measured during the compression process at 200 K. However, when we increased the temperature to around 1500 K using laser-heating technique, the fcc NiH suddenly changed to a new phase. By invoking the structure search calculations, we can identify this new phase as Ni_2H_3 with a $C2/m$ structure. The XRD pattern shows many peaks characteristic to the monoclinic $C2/m$ structure as shown in Fig. 2, which also shows the Le Bail fit of the XRD data at 57 GPa. The fit is of good quality and nearly all the peaks can be indexed to the predicted $C2/m$ structure. During the decompression process, Ni_2H_3 stayed stable at pressures above 17 GPa at the temperature around 200 K, thus the equation of state was measured during the decompression. We were able to synthesize the Ni_2H_3 phase at 83.5 GPa by laser heating method in another experimental run as a major phase quenched from the high temperature produced by laser heating (the x-ray pattern is shown in the supplementary materials). The Ni_2H_3 phase is also stable at ambient temperature under high pressure. However, we do not find the theoretically predicted NiH_2 phase in our reaction

products. We also compared the measured lattice parameters with the theoretical calculations at high pressure as shown in Figure. 3. The measured lattice parameters match quite well the theoretically predicted ones, thus confirming the validity of the suggested structure of Ni_2H_3 .

We can plot the volume per Ni atom ($V/(\text{Ni atom})$) as a function of pressure for Ni, NiH and Ni_2H_3 as shown in Figure.4. The blue and red solid lines are Birch-Murnaghan fitting results for NiH and Ni_2H_3 , respectively. The equation of state of NiH is consistent with extrapolated equation of state from the previous measurements (blue dashed line) taken below 4 GPa [29]; The fitted V_0 parameter of NiH is in close agreement with the previous experiment[29,30]. The small difference is possibly due to the different fitting region of the measured data. Since our data were measured in the higher pressure range, we have obtained larger error bars for V_0 in comparison to the previous studies. We notice that the fitting results are sensitive to the B'_0 , thus it is expected that the B_0 values should differ from the previous result. The red dashed line is the DFT calculation result for Ni_2H_3 . It is clear that the DFT calculation is quite consistent with the experimental data. The significant increase of $V/(\text{Ni atom})$ agrees with the formation of Ni_2H_3 . We list the fitting parameters in Table I. At 60 GPa, $V(\text{NiH})-V(\text{Ni})=1.53 \text{ \AA}^3$ thus the volume expansion for each H atom is $1.53 \text{ \AA}^3$, however, the $V/(\text{Ni atom})$ of Ni_2H_3 is about $11.77 \text{ \AA}^3$, about $1.2 \text{ \AA}^3$ larger than for NiH. It is a common practice that the hydrogen content of the most of the hydrides synthesized recently and characterized by x-ray diffraction is estimated based on the assumptions about extra volume ΔV_H added by each hydrogen atom. However, there is no unambiguous procedure, which would provide the value of ΔV_H for each particular case. Actually, ΔV_H may depend on the element (Fe, Ni, Co,...), on the actual crystal structure (depending on the site in the crystal accommodating the hydrogen atom), and on the nature of the bonding (covalent, ionic, or metallic). For metallic bonding, a great summary of ΔV_H values in transition metal compounds is given in the paper by Fukai [31]. The most common value $\Delta V_H^a \sim 2.8(\pm 0.2) \text{ \AA}^3$ is found for hydrogen sites in many hydride structures. On the other hand, the values $\Delta V_H^b \sim 2.2(\pm 0.2) \text{ \AA}^3$ have been reported in octahedral interstitial sites, in the fcc Fe-D system [32], and in the fcc Ni-Fe-H and Ni-Fe-D systems [33], which are most appropriate for comparison with the fcc NiH structure. The $\Delta V_H = V_0(\text{NiH}) - V_0(\text{Ni}) = 2.24(0.15) \text{ \AA}^3$ from our data (Table 1) at ambient pressure, and it compares reasonably well to similar values from A. Machida et al. [32] and Antonov et al. [33] in the fcc iron and nickel-iron alloys. On the other hand, the ambient pressure value ΔV_H for Ni_2H_3 equals to $(V_0(\text{Ni}_2\text{H}_3) - V_0(\text{Ni}))/1.5 = 2.89 \text{ \AA}^3$, which is close to the value $\Delta V_H^a = 2.8(\pm 0.2) \text{ \AA}^3$ compiled by Fukai [31] for the most of the transition metal hydrides. For this reason we believe that the synthesized Ni_2H_3 phase could be close to the stoichiometric composition. Further studies are required for clarifying the hydrogen composition in Ni_2H_3 and in other recently reported hydrides.

In order to explore the physical properties of Ni_2H_3 , we calculated the electronic states of the stable structure for Ni_2H_3 at 80 GPa as shown in Figure 5. The band structure shows that Ni_2H_3 exhibits metallic properties at 80 GPa with two bands apparently crossing the Fermi level. We calculated the atomic orbital-projected density of states (DOS) of the Ni and H atoms (colored curves in Figure 5). Clearly, H atoms contribute only to the deep energy levels (below -5 eV). The density of states at the Fermi level ($N(E_F)$) is 0.23 states/eV. Please note that contributions from Ni *d*-orbitals at the Fermi level (the purple curve) dominate the electron DOS, whereas H atom *s*-orbital contribution is negligible. In addition, we have calculated the electron-phonon coupling for C2/m- Ni_2H_3 structure and we found the superconducting transition temperature is close to 0 K (Calculated electron-phonon coupling parameter $\lambda=0.2$, and $T_c=0.11$ mK). We calculated also the DOS for NiH_2 at 80 GPa (Fig. S2). The calculated DOS shows features

very similar to the Ni_2H_3 . The contributions from Ni d -orbitals dominate the electron DOS and H atom s -orbital contributions are negligible as well.

The presence of different types of hydrogen can be rationalized based on the effective number of electrons contributed by the Ni atoms and accepted by each H_2 molecule. Because H_2 already had a filled σ bond, the added electrons reside in the antibonding σ^* orbitals, which weakens the H-H bond (i.e., lengthened the H-H bond length) and eventually results in complete dissociation. In order to investigate the electron transfer between Ni and H atoms, we have subsequently performed a topological analysis of the static electron density for Ni_2H_3 and NiH_2 through Bader's quantum theory of atoms-in-molecules (AIM), which has been successfully applied to many systems [34]. In the AIM theory, an atom within a solid is defined through the "zero-flux" condition of the electron density gradient $\nabla\rho(r)$. The results indicate that there is a loss of electron charge in the amount of 0.35e per Ni atom and a gain of -0.23e per H atom in the $C2/m$ - Ni_2H_3 structure. For NiH_2 structure, there corresponding numbers are 0.42e per Ni atom and -0.21e per H atom. These results indicate that the charge transfer plays a key role in stabilizing the structures of the Ni_2H_3 and NiH_2 at high pressures.

Discussion and conclusion

The element Ni stays ferromagnetic at room temperature up to multimegabar pressures [35]. However, the fcc-NiH becomes paramagnetic due to modification of the 3d band, and a significant shift of the Fermi energy E_F caused by the hydrogenation. The DFT calculation indicates that Ni_2H_3 is also nonmagnetic due to the significant modification of the electronic structure, however, no superconductivity (or very low T_C) was predicted.

The phonon properties are important to determine the dynamic stability of materials at high pressures. We employed the supercell approach to compute the interplanar force constants required for the calculations of phonon dispersion curves, which were computed from finite displacements of the atoms according to the crystal symmetry. The Hellmann-Feynman forces and total energies were calculated. Once the force constant is determined, the phonon frequency at selected q points along the symmetry lines in the Brillouin zone can be calculated. We calculated phonon dispersion curves for Ni_2H_3 at 80 GPa, which are shown in Fig. 6. There are no imaginary frequencies found for this structure indicating its dynamic stability at these pressures. The highest phonon frequencies are well below the molecular H_2 vibron range, and must belong to the single hydrogen atoms.

It is well known that the ferromagnetic elements Fe, Co, Ni show many similarities, being the neighboring elements in the Periodic Table with similar, but not identical chemical properties. FeH, CoH, and NiH can be synthesized by the direct reaction with H_2 fluid under several gigapascal pressure, although their phase diagrams for Me-H system (Me=Fe, Co, Ni) could be very different in few GPa range[15]. Theoretical calculations indicate stable phases of NiH_2 and CoH_2 with structure similar to FeH_2 [36], which may indicate similarity of the corresponding Me-H phase diagrams in the pressure range around 50-60 GPa. However, our calculations and experimental results indicate that Ni-H system behaves differently in comparison to the Fe-H system. In the experiment, we did not synthesize the theoretically predicted NiH_2 phase, but synthesized instead a monoclinic Ni_2H_3 , which is stable at high pressures and was not observed in the Fe-H system [10]. In addition, cubic FeH_3 can be also formed at high pressures around 87 GPa [10] and isostructural CoH_3 was also predicted to be stable by the theoretical calculations in that pressure range. Despite these predicted similarities, only Ni_2H_3 can be synthesized up to 83.5 GPa for NiH_x . In comparison to iron, Ni seems to be

reluctant to form NiH_x with higher hydrogen content, and preserves distinct chemical properties to very high pressures. However, there is a possibility that we missed the conditions required for the synthesis of the theoretically predicted NiH_2 phase in our experiments. Further experiments may clarify if that phase could be stabilized and what would be the required P-T path for such synthesis.

It is believed that the core of our planet is mainly composed of iron-nickel alloy (about 90% Fe) with a dissolution of one or more lighter elements [37-39]. Hydrogen has been proposed as a possible light element in the Earth's core. Thus, both FeH_x and NiH_x can be formed in the deep Earth. Distinct chemical properties of Fe and Ni with respect to hydride formation may give rise to unexpectedly complicated Fe-Ni-H ternary phase diagram, with phase separation of FeH_x and NiH_x species. Thus, new studies of Fe-Ni-H system at very high pressures would be very desirable.

In conclusion, we synthesized a new nickel hydride Ni_2H_3 phase at high pressures, which we also confirmed by our theoretical DFT calculations. However, we did not observe the theoretically predicted tetragonal phase of NiH_2 . The structure of monoclinic Ni_2H_3 was never observed in the other hydrides. Our results show completely different hydride phases quenched in a laser heating experiment for the Fe-H and the Ni-H systems below 84 GPa, which is at odds with the theoretical predictions. The successful synthesis of the new nickel hydride Ni_2H_3 at high pressure confirms the trend for an increase of hydrogen content in hydrides with the increasing pressure. New polyhydrides of nickel with higher hydrogen content may exist at even higher pressures, and further experiments are needed to clarify if the theoretically predicted NiH_2 phase could be stabilized at high pressures and what would be the required P-T path for such synthesis.

Our results indicate that the Fe-Ni alloy may exhibit quite different hydride phases at high pressures in comparison to pure Fe, as far as the chemistry of Fe, Ni, and hydrogen is concerned. These results may be crucial for understanding the implications of hydride phases for the chemistry of the planetary interiors. Further work is required to find out what high-pressure phases are stable in the Fe-Ni-H ternary system at high pressure and temperature conditions.

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Bibliography

- [1] V. V. Struzhkin, *Physica C: Superconductivity and its Applications* **514**, 77 (2015).
- [2] A. P. Drozdov, M. I. Erements, I. A. Troyan, V. Ksenofontov, and S. I. Shylin, *Nature* **525**, 73 (2015).
- [3] I. Troyan, A. Gavriluk, R. Ruffer, A. Chumakov, A. Mironovich, I. Lyubutin, D. Perekalin, A. P. Drozdov, and M. I. Erements, *Science* **351**, 1303 (2016).

- [4] D. Duan *et al.*, Scientific Reports **4**, 6968 (2014).
- [5] Y. Li, J. Hao, H. Liu, Y. Li, and Y. Ma, The Journal of Chemical Physics **140**, 174712 (2014).
- [6] V. V. Struzhkin, D. Y. Kim, E. Stavrou, T. Muramatsu, H.-k. Mao, C. J. Pickard, R. J. Needs, V. B. Prakapenka, and A. F. Goncharov, Nature Communications **7**, 12267 (2016).
- [7] C. Pépin, P. Loubeyre, F. Occelli, and P. Dumas, Proceedings of the National Academy of Sciences **112**, 7673 (2015).
- [8] C. M. Pépin, G. Geneste, A. Dewaele, M. Mezouar, and P. Loubeyre, Science **357**, 382 (2017).
- [9] T. Scheler, M. Marqués, Z. Konôpková, C. L. Guillaume, R. T. Howie, and E. Gregoryanz, Physical Review Letters **111**, 215503 (2013).
- [10] C. M. Pépin, A. Dewaele, G. Geneste, P. Loubeyre, and M. Mezouar, Physical Review Letters **113**, 265504 (2014).
- [11] M. Wang, J. Binns, M.-E. Donnelly, M. Peña-Alvarez, P. Dalladay-Simpson, and R. T. Howie, The Journal of Chemical Physics **148**, 144310 (2018).
- [12] M. A. Kuzovnikov, H. Meng, and M. Tkacz, Journal of Alloys and Compounds **694**, 51 (2017).
- [13] M. A. Kuzovnikov, M. Tkacz, H. Meng, D. I. Kapustin, and V. I. Kulakov, Physical Review B **96**, 134120 (2017).
- [14] B. Li, Y. Ding, D. Y. Kim, R. Ahuja, G. Zou, and H.-K. Mao, Proceedings of the National Academy of Sciences **108**, 18618 (2011).
- [15] Y. Fukai, The Metal-Hydrogen System, 2nd ed. (Springer-Verlag, Berlin/Heidelberg, 2005).
- [16] V. B. Prakapenka, A. Kubo, A. Kuznetsov, A. Laskin, O. Shkurikhin, P. Dera, M. L. Rivers, and S. R. Sutton, High Pressure Research **28**, 225 (2008).
- [17] Y. Fei, A. Ricolleau, M. Frank, K. Mibe, G. Shen, and V. Prakapenka, Proceedings of the National Academy of Sciences **104**, 9182 (2007).
- [18] C. Prescher and V. B. Prakapenka, High Pressure Research **35**, 223 (2015).
- [19] A. C. Larson and R. B. Von Dreele, Los Alamos National Laboratory Report LAUR **86-748** (1994).
- [20] Y. Wang, J. Lv, L. Zhu, and Y. Ma, Physical Review B **82**, 094116 (2010).
- [21] Y. Wang, J. Lv, L. Zhu, and Y. Ma, Computer Physics Communications **183**, 2063 (2012).
- [22] J. Lv, Y. Wang, L. Zhu, and Y. Ma, Physical Review Letters **106**, 015503 (2011).
- [23] L. Zhu, H. Liu, C. J. Pickard, G. Zou, and Y. Ma, Nature Chemistry **6**, 644 (2014).
- [24] L. Wang *et al.*, Inorganic Chemistry **57**, 181 (2018).
- [25] J. P. Perdew, K. Burke, and M. Ernzerhof, Physical Review Letters **77**, 3865 (1996).
- [26] G. Kresse and J. Furthmüller, Physical Review B **54**, 11169 (1996).
- [27] G. Kresse and D. Joubert, Physical Review B **59**, 1758 (1999).
- [28] H. J. Monkhorst and J. D. Pack, Physical Review B **13**, 5188 (1976).
- [29] N. Ishimatsu *et al.*, Physical Review B **86**, 104430 (2012).
- [30] V. E. Antonov, Journal of Alloys and Compounds **330-332**, 110 (2002).
- [31] Y. Fukai, Journal of the Less Common Metals **101**, 1 (1984).
- [32] A. Machida *et al.*, Nature Communications **5**, 5063 (2014).
- [33] V. E. Antonov, M. Baier, B. Dorner, V. K. Fedotov, G. Grosse, A. I. Kolesnikov, E. G. Ponyatovsky, G. Schneider, and F. E. Wagner, Journal of Physics: Condensed Matter **14**, 6427 (2002).
- [34] R. F. W. Bader, Chemical Reviews **91**, 893 (1991).
- [35] I. Sergueev *et al.*, Physical Review Letters **111**, 157601 (2013).
- [36] H. Yu, W. Lao, L. Wang, K. Li, and Y. Chen, Physical Review Letters **118**, 137002 (2017).

- [37] H. K. Mao, Y. Wu, L. C. Chen, J. F. Shu, and A. P. Jephcoat, Journal of Geophysical Research: Solid Earth **95**, 21737 (1990).
- [38] R. Jeanloz, Annual Review of Earth and Planetary Sciences **18**, 357 (1990).
- [39] F. Birch, Journal of Geophysical Research **57**, 227 (1952).

Table I. The volume per formula unit at ambient pressure $V/(\text{Ni atom})$, the bulk modulus B_0 , the pressure derivative of the bulk modulus B'_0 as derived from fitting results measured around 200 K by using the B-M equation of state. Numbers between parentheses represent fitting or published errors bars.

	Crystal structure	$V_0/(\text{Ni atom})$ ($\text{\AA}^3$)	B_0 (GPa)	B'_0	Reference
Ni	fcc	10.96(0.02)	181	5.2	[29]
NiH	fcc	13.20(0.15)	206(19)	2.6(0.6)	This work
		13.14(0.02)	176(2)	4(fixed)	[29]
Ni ₂ H ₃	C2/m	15.29(0.2)	148(15)	3.4(0.6)	This work

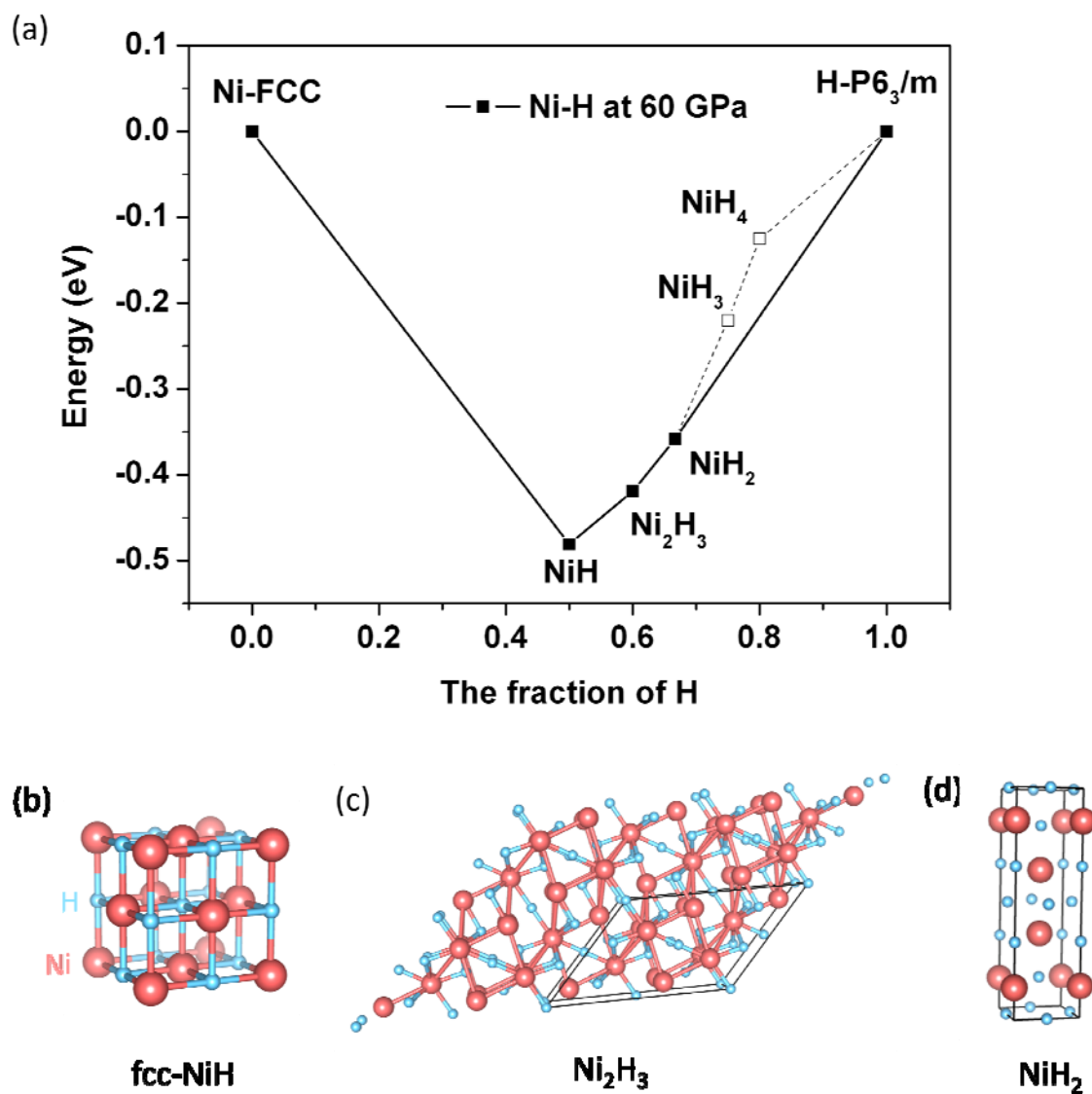


Figure 1. (a) The calculated convex-hull of Ni-H system at 60 GPa. NiH, Ni₂H₃ and NiH₂ are thermodynamically stable at 60 GPa. We did not consider the zero-point energy in the calculated formation enthalpy of the Ni-H phases. The representation of structures for the three theoretically predicted Nickel hydrides at high pressure: fcc-NiH (b), C2/m-Ni₂H₃ (c), and I4/mmm-NiH₂ (d).

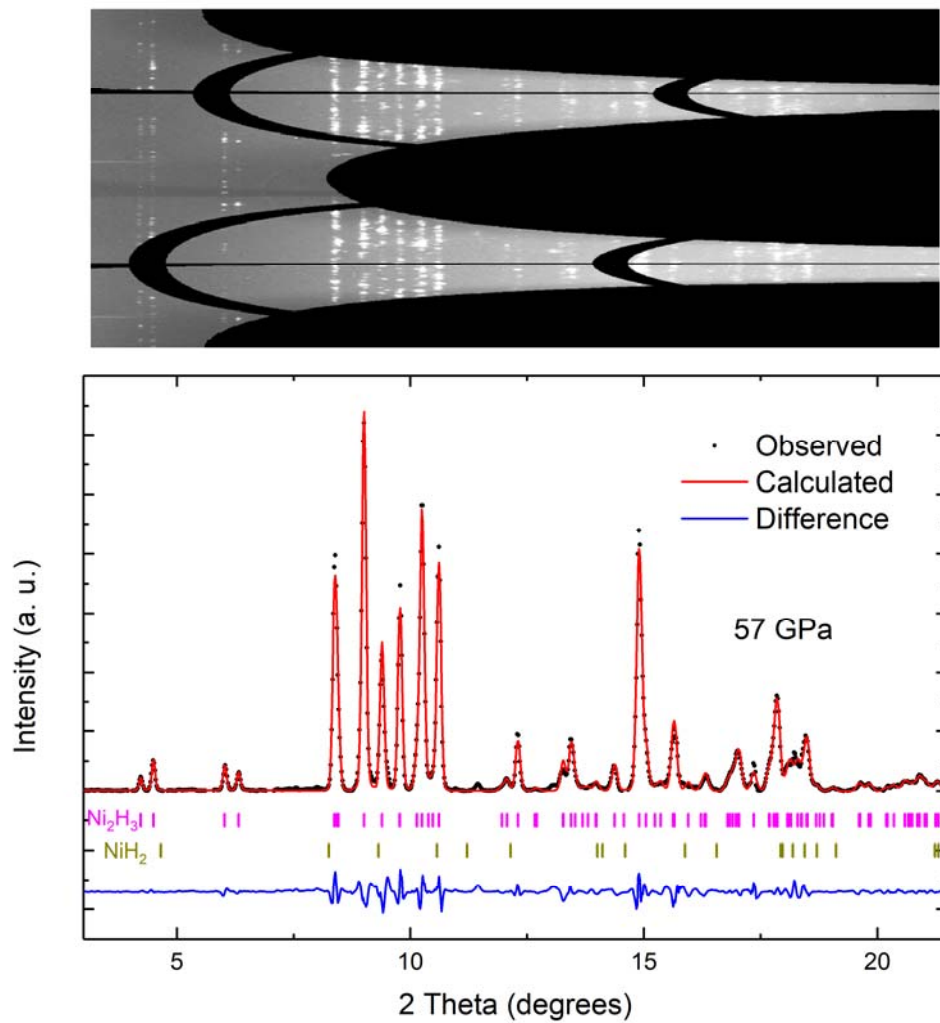


Figure 2. The upper panel shows the cake-type image of the two dimensional x-ray diffraction pattern for Ni_2H_3 at 57 GPa with temperature around 200 K. The lower panel shows the Le Bail fit result for the integrated pattern by using the theoretically predicted structure model (C2/m): nearly all the peaks can be fit well using theoretical structural model ($\lambda=0.3344 \text{ \AA}$).

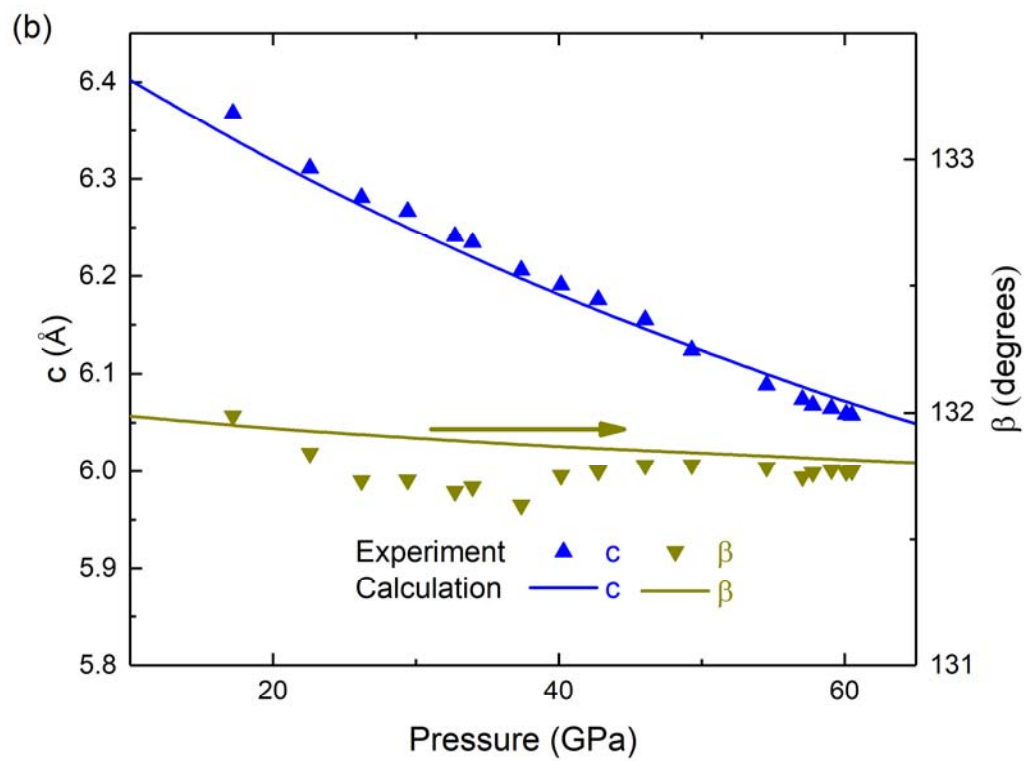
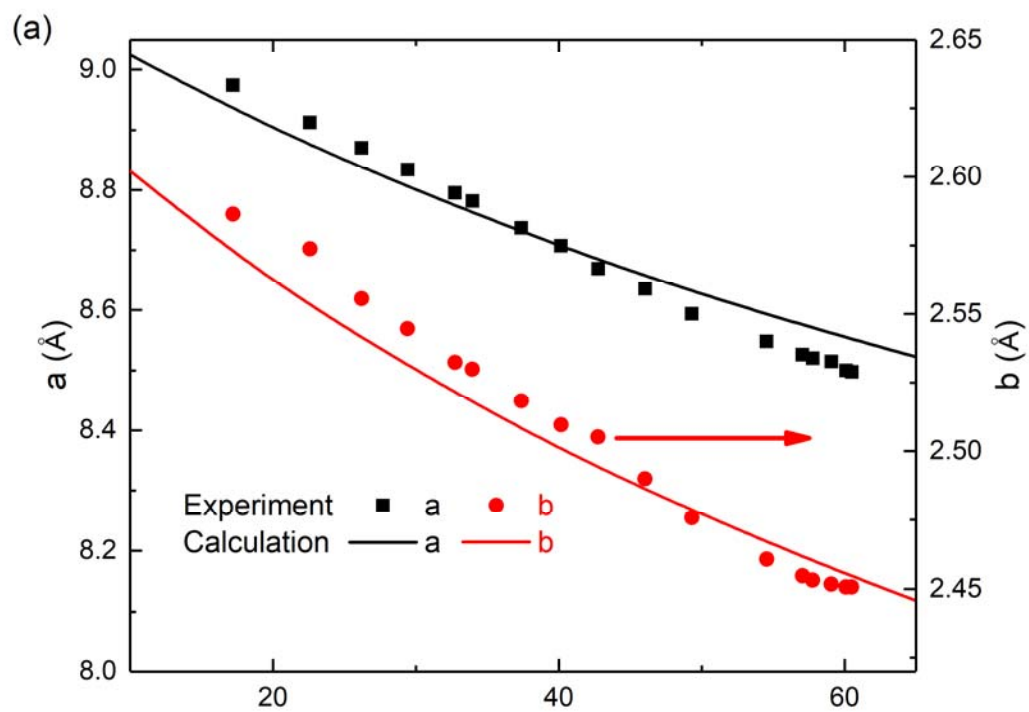


Figure 3. Comparison of the experimental lattice parameters measured around 200 K and the theoretical ones resulting from the DFT calculations for the monoclinic Ni_2H_3 phase at various pressures.

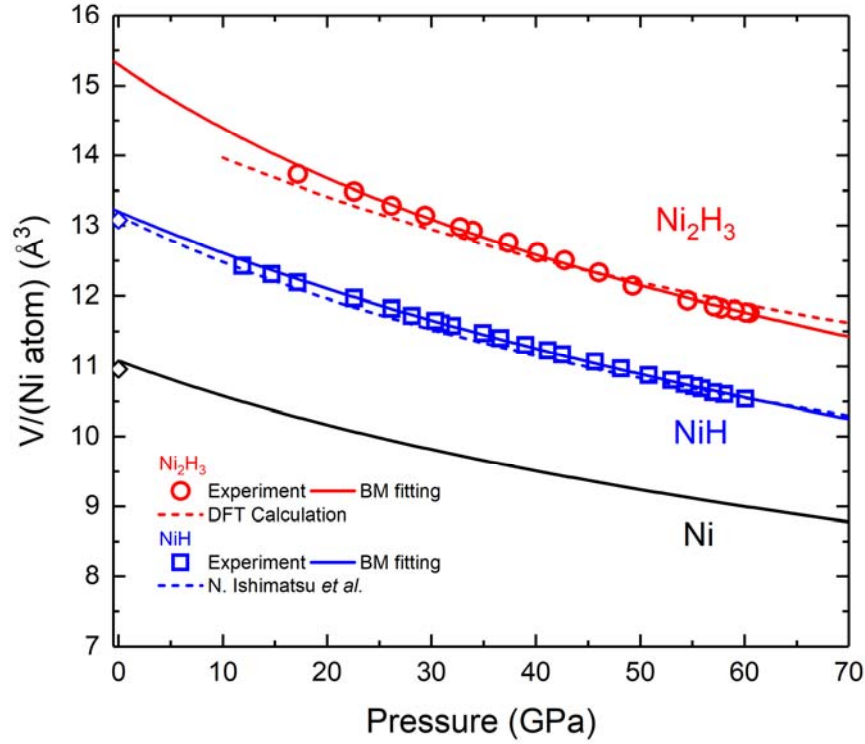


Figure 4. The volume per Ni atom as a function of pressure for Nickel hydrides measured at 200 K. NiH was measured during the compression process. For Ni_2H_3 , the DFT calculations (red dashed line) are consistent with the experimental results. The solid lines represent the BM fit results as given in Table. I. The blue dashed line indicates the BM fitting result of NiH data at ambient temperature obtained by N. Ishimatsu *et al* below 4 GPa [29]. The blue and black diamond represent the V_0 value for NiH and Ni measured previously.

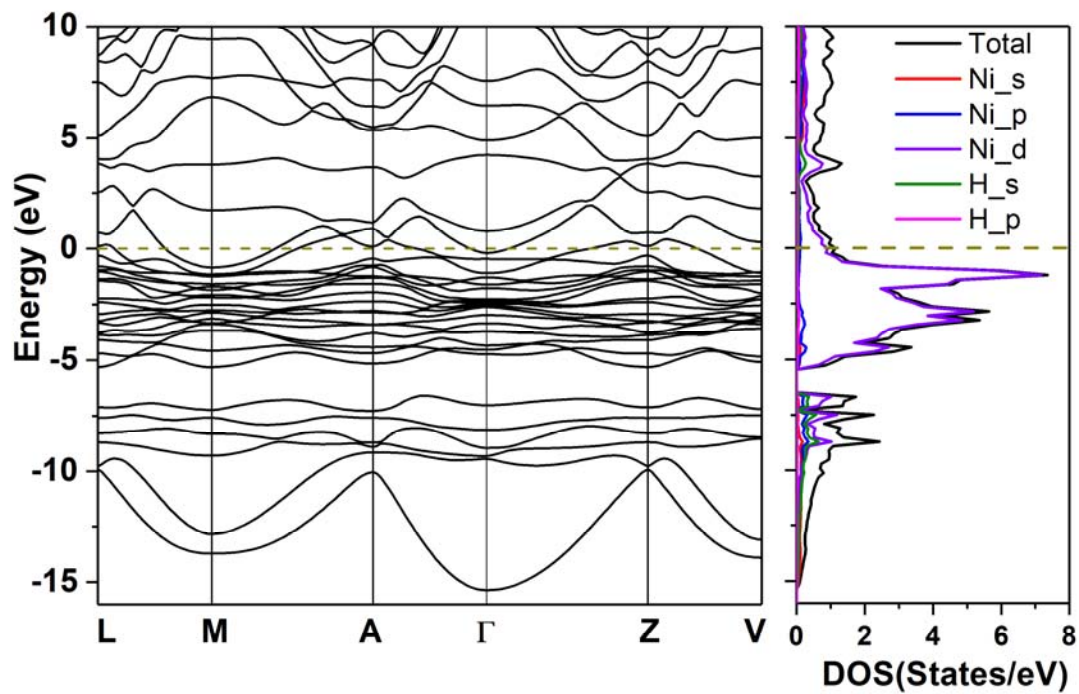


Figure 5. The calculated band structure and density of states for predicted $C2/m$ - Ni_2H_3 structure at 80 GPa. The calculation indicates Ni_2H_3 is a metal and its Fermi surface is dominated by the Ni d - orbitals.

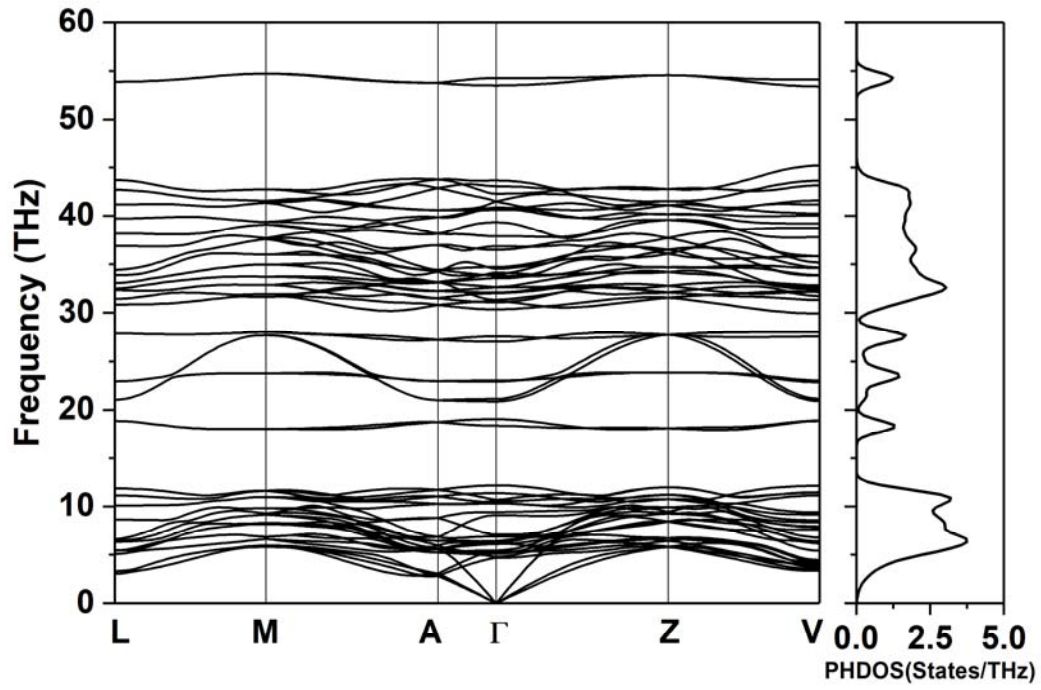


Figure 6. The calculated phonon dispersion for the predicted C2/m-Ni₂H₃ at 80 GPa. The absence of any imaginary frequency modes in the whole Brillouin zone suggests the dynamical stability of C2/m-Ni₂H₃ at high pressures.