

FIRST PRINCIPLES INVESTIGATION OF THE H-La-Ni-Sn SYSTEM

^{1,2}Kateřina DOČKALOVÁ, ^{1,2}Jana PAVLŮ, ¹Martin FRIÁK, ¹Ondřej ZOBAČ

¹*Institute of Physics of Materials, v. v. i., Czech Academy of Sciences, Brno, Czech Republic, EU,
dockalova@ipm.cz, pavlu@ipm.cz, friak@ipm.cz, zobac@ipm.cz,*

²*Department of Chemistry, Faculty of Science, Masaryk University, Brno, Czech Republic, EU,
pavlu@chemi.muni.cz*

<https://doi.org/10.37904/metal.2026.5305>

Abstract

Investigating hydrogen sorption in hydride-forming materials is essential for advancing a wide range of industrial technologies, particularly hydrogen storage. Among such materials, LaNi₅ is a well-established candidate due to its ability to form multiple hydride phases. In this work, density-functional-theory calculations, as implemented in the VASP code, were employed to investigate the structural, energetic, and magnetic properties of hydrogen-doped LaNi₅ structures. First, the equilibrium lattice parameters of the pristine LaNi₅ were determined. Subsequently, a series of hydrogenated configurations was constructed by introducing hydrogen atoms into interstitial sublattices of the host structure, specifically the 2b, 6c (in two distinct configurations), and 12d sites. In these models, the selected sublattices were assumed to be fully occupied by hydrogen. An additional configuration was also considered, in which hydrogen simultaneously occupied all of the above-mentioned interstitial sites. Furthermore, the thermodynamic end-member LaSn₅H₆ was investigated using first-principles calculations. The results obtained can serve as input for thermodynamic modeling within the CALPHAD (CALculation of PHase Diagrams) framework. Our results provide insight into the effect of hydrogen incorporation on the structural stability and magnetic properties of LaNi₅-based hydrogen storage materials.

Keywords: hydrogen storage, H-La-Ni-Sn, LaNi₅, LaNi₅H_y, LaSn₅H₆, DFT, VASP

1. INTRODUCTION

The growing demand for sustainable energy storage has intensified the search for efficient hydrogen storage materials. Among these, LaNi₅ stands out as a benchmark system due to its favorable hydrogen-absorption energetics, fast kinetics, and reversibility. However, the rational design of such materials for industrial applications and the accurate prediction of their macroscopic behavior require a detailed understanding of their atomic-scale properties. In this context, first-principles calculations provide a powerful tool for investigating the preferred hydrogen positions in the LaNi₅ structure. The theoretical study of hydride structures is essential, as the experimental determination of hydrogen positions using X-ray diffraction remains challenging. In hydrides of electron-rich metals, hydrogen atoms are effectively screened by the surrounding electron density, which significantly limits their experimental detectability [1].

The primitive cell of LaNi₅ is commonly described using the *P6/mmm* (No. 191) space group, corresponding to the CaCu₅-type structure. In Wyckoff notation, La atoms occupy the 1a sites, while Ni atoms are distributed over the 3g and 2c sites [2]. Hydrogen atoms occupy interstitial sites within the LaNi₅ structure. Two of the most experimentally and theoretically investigated LaNi₅-hydride phases are LaNi₅H₆ and LaNi₅H₇. LaNi₅H₆ is typically described using the *P31m* (No. 157) space group or *P3m1* (No. 156), where three hydrogen atoms fully occupy 3c sites and three additional hydrogen atoms partially occupy 6d sites, without requiring expansion

of the parent LaNi_5 cell [3]. In contrast, the description of the LaNi_5H_7 hydride requires a doubling of the unit cell along the c -axis, resulting in the $\text{La}_2\text{Ni}_{10}$ supercell (plus 14 H atoms). This phase is typically described by the $P6_3mc$ space group (No. 186). In this configuration, six hydrogen atoms fully occupy $6c^1$ and $6c^2$ sites, while the remaining two hydrogen atoms fully occupy the $2b$ lattice sites [4]. However, to achieve a more comprehensive understanding of the hydrogen storage capacity of LaNi_5 , it is necessary to investigate additional hydride configurations. Within the $\text{La}_2\text{Ni}_{10}$ supercell described by the $P6_3mc$ space group, four types of interstitial sites are available for hydrogen incorporation: $2b$, $6c^1$, $6c^2$, and $12d$ (see **Figure 1**).

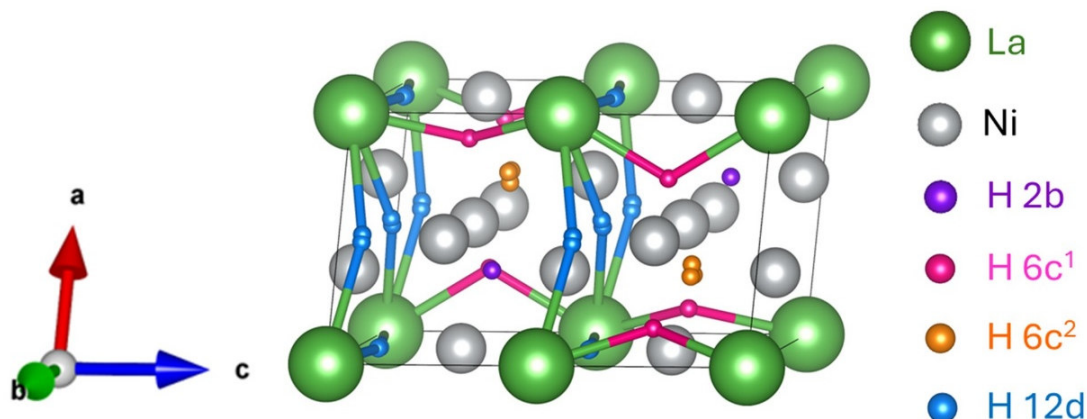


Figure 1 Interstitial lattice sites for hydrogen incorporation in LaNi_5 ($P6_3mc$ space group)

The amount and distribution of hydrogen within the LaNi_5 structure play a crucial role in determining its properties, including magnetism, thermodynamic stability, and structural characteristics. Therefore, in this work, we systematically investigate a series of LaNi_5 hydride configurations, in which hydrogen fully occupies each of the aforementioned sublattices individually, as well as all available interstitial sites simultaneously.

Industrially, the hydrogen sorption and desorption characteristics of LaNi_5 can be improved through the partial substitution of nickel atoms. In this study, we focus on tin as the substituent. The resulting solid solutions, $\text{LaNi}_{5-x}\text{Sn}_x$, exhibit enhanced stability compared to the parent LaNi_5 , along with reduced sorption/desorption equilibrium pressures and an increased hydrogen absorption rate [5]. The substitution of nickel by tin affects both the magnetic and structural properties of the material by altering its electronic structure and lattice parameters. In this work, we also investigate the fully Sn-substituted and hydrogenated LaSn_5H_6 phase, which serves as an end-member in the CALPHAD (CALculation of PHase Diagrams) thermodynamic modeling.

2. MODELS AND COMPUTATIONAL METHODOLOGY

Various LaNi_5H_y configurations were constructed by inserting hydrogen atoms into selected interstitial sites of the $\text{La}_2\text{Ni}_{10}$ supercell, as illustrated in **Figure 1**. The crystallographic model of $\text{La}_2\text{Ni}_{10}$ was based on the $P6_3mc$ space group. In this work, the full occupation of each type of interstitial site by hydrogen atoms was systematically investigated, leading to the following name convention of the studied configurations: $\text{LaNi}_5\text{-}2b$, $\text{LaNi}_5\text{-}6c^1$, $\text{LaNi}_5\text{-}6c^2$, $\text{LaNi}_5\text{-}12d$, and $\text{LaNi}_5\text{-all}$ (with hydrogen occupying $2b$, $6c^1$, $6c^2$, and $12d$ sublattices, respectively). Additionally, the experimentally reported LaNi_5H_7 structure can be interpreted as a combination of the $\text{LaNi}_5\text{-}2b$, $\text{LaNi}_5\text{-}6c^1$, and $\text{LaNi}_5\text{-}6c^2$ configurations.

The LaSn_5H_6 structure was constructed from the LaNi_5H_6 by the full substitution of nickel atoms with tin atoms (see **Figure 2**). However, because tin has a larger atomic radius than nickel, the original cell was expanded to accommodate the increased volume.

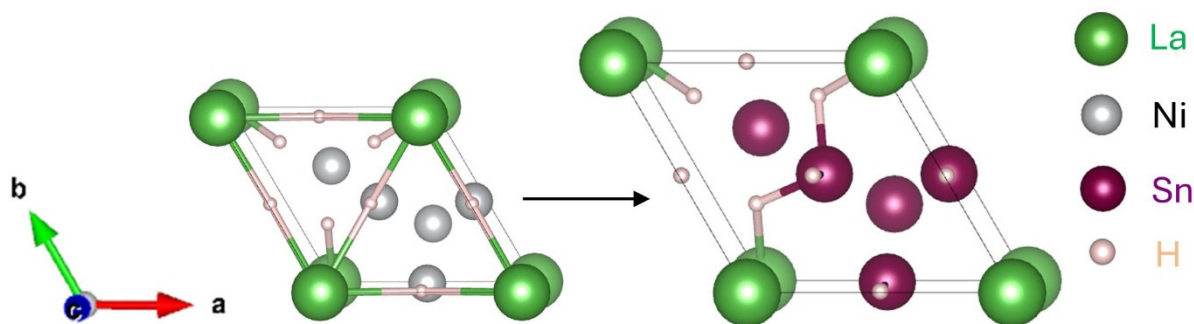


Figure 2 LaNi₅H₆ (left) and LaSn₅H (right) phases created by the full substitution of the nickel by tin atoms

The first-principles calculations employed in this work were performed within the Density Functional Theory (DFT) framework using the Vienna Ab initio Simulation Package (VASP) [6,7]. The exchange-correlation interactions were described using the Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) [8,9] parametrization. The Projector-Augmented Wave (PAW) pseudopotentials [10,11] with the suffixes: H_h, Ni_sv_GW, Sn_sv_GW and La_GW from the potpaw_PBE.64 VASP database were employed. The kinetic energy cutoff for the plane-wave basis set was set to 870 eV. The Brillouin zone was sampled using a Γ -centered k-point mesh, with the k-point spacing (KSPACING) of 0.013 nm⁻¹ for LaNi₅ and LaNi₅H₆, 0.019 nm⁻¹ for LaNi₅H₇, 0.011 nm⁻¹ for LaSn₅H₆, and 0.02 nm⁻¹ for LaNi₅-2b, LaNi₅-6c¹, LaNi₅-6c², LaNi₅-12d, and LaNi₅-all. The chosen values for the energy cutoff and k-point sampling were determined from convergence tests, yielding an accuracy of 5×10^{-5} eV/at. Based on the metallic character of LaNi₅ hydrides, the Methfessel-Paxton smearing scheme was applied.

3. RESULTS

Hydrogenation can significantly influence the magnetic properties of materials. According to our calculations, the LaNi₅ phase exhibits a ferrimagnetic ordering, with magnetization primarily originating from nickel 3d electrons. We investigated the evolution of magnetic properties and unit-cell expansion upon hydrogen incorporation into different lattice sites. The results are summarized in **Table 1** and illustrated in **Figure 3**.

Table 1 Magnetic and volumetric properties of LaNi₅H_y configurations and the pristine LaNi₅ phase

Phase/Configuration	X _H (at. %)	Magnetic state	ΔV (%)
LaNi ₅	0.00	Ferrimagnetic	-
LaNi ₅ -2b	14.29	Ferrimagnetic	5.34
LaNi ₅ -6c ¹	33.33	Ferrimagnetic	9.65
LaNi ₅ -6c ²	33.33	Nonmagnetic	10.64
LaNi ₅ -12d	50.00	Nonmagnetic	18.71
LaNi ₅ H ₇	53.85	Ferrimagnetic	25.51
LaNi ₅ -all	68.42	Nonmagnetic	45.71

The incorporation of hydrogen atoms into all available interstitial sites leads to a lattice expansion of 45.71 % relative to the pristine LaNi₅ cell, accompanied by a loss of ferrimagnetic ordering. However, no simple correlation between hydrogen concentration and magnetic properties is observed, suggesting that magnetism is governed not only by hydrogen content but also by its site-specific interactions with the Ni sublattice.

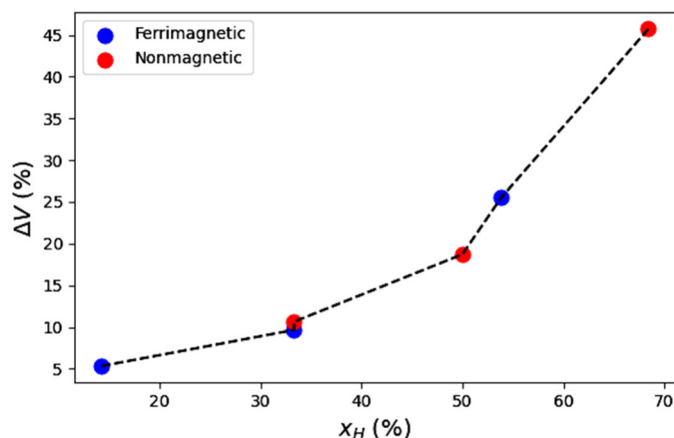


Figure 3 Lattice expansion and the magnetic state as a function of hydrogen content

Likewise, the lattice expansion exhibits a pronounced nonlinear dependence on hydrogen content, indicating that the volume change is strongly governed by the type of occupied interstitial sites. In particular, distinct local environments (e.g., 2b, 6c, and 12d sites) induce different lattice distortions and electronic perturbations, which affect structural expansion and magnetic state changes in a non-uniform manner.

Ferrimagnetic behavior is preserved only in $\text{LaNi}_5\text{-}2\text{b}$ and $\text{LaNi}_5\text{-}6\text{c}^1$ configurations, as well as in the LaNi_5H_7 phase. Notably, although the $\text{LaNi}_5\text{-}6\text{c}^1$ and $\text{LaNi}_5\text{-}6\text{c}^2$ configurations have the same hydrogen content, their magnetic properties differ: $\text{LaNi}_5\text{-}6\text{c}^1$ remains ferrimagnetic, whereas $\text{LaNi}_5\text{-}6\text{c}^2$ is nonmagnetic. The magnetic moment per cell can be obtained from the difference between the spin-up and spin-down electronic densities, as illustrated in the density-of-states plots (see **Figure 4**).

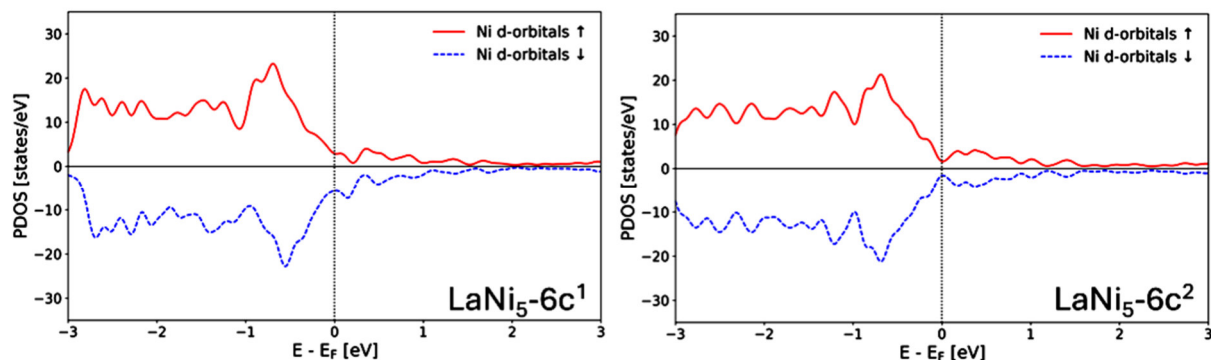


Figure 4 Projected Density Of States (PDOS) of Ni 3d orbitals for $\text{LaNi}_5\text{-}6\text{c}^1$ and $\text{LaNi}_5\text{-}6\text{c}^2$ configurations

The observed difference in magnetic behavior can be attributed to the distinct local arrangement of hydrogen atoms, which modifies the Ni-H hybridization and the distribution of Ni 3d states near the Fermi level. In the $\text{LaNi}_5\text{-}6\text{c}^1$ configuration, the electronic structure favors spin polarization, as evidenced by the asymmetry of Ni 3d states at the Fermi level. In contrast, in $\text{LaNi}_5\text{-}6\text{c}^2$, a stronger or more symmetric Ni-H interaction likely redistributes Ni 3d states, leading to a spin-degenerate electronic structure and suppression of magnetism.

Within this study, we also investigated structural changes induced by tin substitution, with particular emphasis on variations in atomic arrangements in the hydride phases. To this end, the Radial Distribution Function (RDF) was employed to analyze the atomic spatial distribution. This approach further enabled us to examine the redistribution and preferred positions of hydrogen atoms within the structure.

The full substitution of nickel by tin leads to a significant lattice expansion, with the unit-cell volume increasing to approximately 136.77% relative to the original structure. This expansion arises from the larger atomic radius of tin compared to nickel and is associated with substantial modifications of interatomic distances and local structural rearrangements, as illustrated schematically by the RDF in **Figure 5**. Both LaNi_5H_6 and LaSn_5H_6 phases are nonmagnetic. Despite these structural changes, the LaSn_5H_6 phase retains the same crystallographic symmetry as LaNi_5H_6 , namely the $P3m1$ space group.

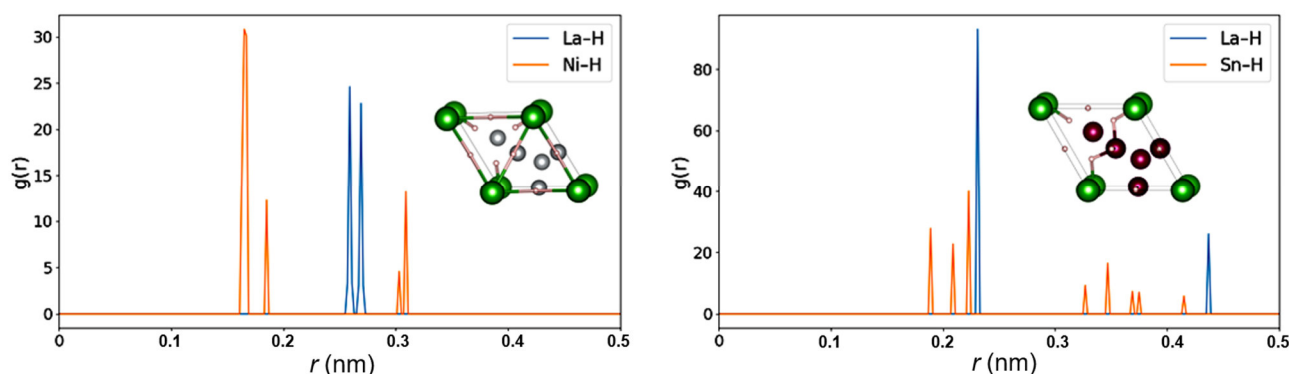


Figure 5 Radial distribution function $g(r)$ for LaNi_5H_6 (left) and LaSn_5H_6 (right)

The Ni-H bond lengths in LaNi_5H_6 exhibit a bimodal distribution, with shorter bonds (0.164–0.167 nm) corresponding to stronger Ni-H hybridization and longer bonds around 0.186 nm, reflecting weaker interactions in less favorable geometries. This indicates the presence of multiple local bonding environments within the structure. Additional features at ~ 0.3 nm arise from second-nearest-neighbor correlations and reflect long-range ordering rather than direct bonding. The La-H distances are longer (~ 0.260 – 0.268 nm), indicating weaker and more ionic interactions that primarily contribute to lattice expansion rather than direct bonding stabilization. In contrast, LaSn_5H_6 exhibits significantly broader and generally longer bond-length distributions, indicating substantial structural distortion and weaker, less uniform bonding. La-H distances extend up to ~ 0.437 nm, while Sn-H interactions are more dispersed, reflecting the absence of well-defined local environments compared to the Ni-based system.

4. CONCLUSIONS

First-principles calculations were employed to investigate the relationships among lattice expansion, magnetic properties, and hydrogen content in LaNi_5 -based hydrides. The lattice expansion exhibits a nonlinear dependence on hydrogen content and is strongly influenced by specific hydrogen lattices. Similarly, no direct correlation between magnetic arrangement and hydrogen content was observed. Configurations $\text{LaNi}_5\text{-2b}$, $\text{LaNi}_5\text{-6c}^1$, and LaNi_5H_7 remain ferrimagnetic, whereas the other configurations become nonmagnetic. This behavior arises from the sensitivity of Ni 3d states to the local hydrogen environment, where site-dependent Ni-H hybridization modifies the position and spin polarization of electronic states near the Fermi level.

Furthermore, LaNi_5H_6 and LaSn_5H_6 phases are both nonmagnetic. The substitution of Ni atoms by Sn atoms causes the breakdown of the well-defined Ni-H bonding network, replaced by weaker and more dispersed Sn-H and La-H interactions. Consequently, broader and generally longer bond-length distributions are observed, indicating pronounced structural distortion and the absence of well-defined local hydrogen environments.

DATA AVAILABILITY

The VASP input and output files are available under DOI:10.5281/zenodo.19849722.

ACKNOWLEDGEMENTS

This study was created as part of the project No. CZ.02.01.01/00/22_008/0004631 Materials and Technologies for Sustainable Development within the Jan Amos Komensky Operational Program financed by the European Union and from the state budget of the Czech Republic. Computational resources were provided by IT4Innovations National Supercomputing Center, the MetaCentrum, and CERIT-SC under the Project e-INFRA CZ (ID:90254) supported by the Ministry of Education, Youth and Sports of the Czech Republic. Access to CESNET storage facilities provided by the project e-INFRA CZ under the program "Projects of Large Research, Development, and Innovations Infrastructures" (LM2023054) is appreciated. Financial support from the Czech Academy of Sciences via the Praemium Academiae awarded to Martin Friák, from the Institute of Physics of Materials, Czech Academy of Sciences, Brno, Czech Republic, is gratefully acknowledged. The structures were visualized using the VESTA package [12].

REFERENCES

- [1] WOJŃSKA, M., CHODKIEWICZ, M. L., WOŹNIAK, K. Towards accurate and precise positions of hydrogen atoms bonded to heavy metal atoms, *RSC* 2021, vol. 57, pp. 3652–3655.
- [2] WERNICK, J. H. Transition element-rare earth compounds with Cu_5Ca structure. *Acta Crys.* 1959, vol. 12, pp. 662–665.
- [3] FISCHER, P., FURRER, A., BUSCH, G., SCHLAPBACH, L. Neutron scattering investigations of the LaNi_5 hydrogen storage system. *Helv. Phys. Acta.* 1977, vol. 50, pp. 421–430.
- [4] TATSUMI, K., TANAKA, I., INUI, H., TANAKA, K., YAMAGUCHI, M., ADACHI, H. Atomic structures and energetics of $\text{LaNi}_5\text{-H}$ solid solution and hydrides. *Phys. Rev. B.* 2001, vol. 64, pp. 184105.
- [5] BORZONE, E. M., BLANCO, M. V., BARUJ, A., MEYER, G. O. Stability of $\text{LaNi}_{5-x}\text{Sn}_x$ cycled in hydrogen. *Int. J. of Hydrogen Energy.* 2014, vol. 39, pp. 8791–8796.
- [6] KRESSE, G., FURTHMÜLLER, J. Efficient iterative schemes for ab initio total energy calculations using a plane-wave basis set. *Phys. Rev. B.* 1996, vol. 54, pp. 11169.
- [7] KRESSE, G., HAFNER, J. Ab Initio molecular dynamics for liquid metals. *Phys. Rev. B.* 1993, vol. 47, pp. 558.
- [8] PERDEW, J. P., BURKE, K., ERNZERHOF, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 1996, vol. 77, pp. 3865.
- [9] PERDEW, J. P., BURKE, K., ERNZERHOF, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 1997, vol. 78, pp. 1396.
- [10] KRESSE, G., JOUBERT, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B.* 1999, vol. 59, pp. 1758.
- [11] BLOCHL, P.E. Projector augmented-wave method. *Phys. Rev. B.* 1994, vol. 50, pp. 17953.
- [12] MOMMA, K., IZUMI, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.* 2011, vol. 44, pp. 1272–1276.