QUANTUM-MECHANICAL STUDY OF HLaNiSn INTERMETALLIC PHASE

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Abstract

Energy storage remains a central challenge in realizing a complete transition to renewable energy sources, with hydrogen storage emerging as a particularly promising solution. Metal hydrides offer a viable platform due to their high volumetric density of hydrogen and safety. However, further research is needed to identify compositions that combine high hydrogen capacity with fast hydrogen uptake and release at reasonable operating temperatures. The La-Ni-Sn system exhibits notable structural and electronic properties, making it a candidate for hydrogen storage and energy applications. The binary compound $LaNi_5$ and the ternary phase LaNiSn are known to form multiple hydrides, many of which remain poorly characterized. Using a quantum-mechanical approach, this study focuses on the stoichiometric H_1LaNiSn phase, namely its stability, equilibrium properties, phonons, electronic structure and hydrogen absorption behavior. These results offer critical insight into the thermodynamic stability and electronic structure of H_1LaNiSn, enhancing the understanding of its potential in hydrogen storage applications. We determined the ground-state properties, including the lattice parameters, the electronic density of states and the phonon band structure. Additionally, we evaluated the temperature dependencies of key thermodynamic quantities (free energy, entropy and heat capacity) within the harmonic approximation. Importantly, the H_1LaNiSn phase was found to be mechanically stable, supporting its viability as a hydrogen storage material.

Keywords: DFT, H_1LaNiSn, equilibrium structural parameters, phonon band structure, hydrogen

1. INTRODUCTION

Efficient energy storage remains a major challenge in the complete transition to renewable energy sources, with hydrogen storage emerging as a particularly promising solution. Metal hydrides constitute a viable class of materials for this purpose, offering high volumetric density of hydrogen and favorable safety characteristics. However, continued research is essential to discover compositions that balance high hydrogen storage capacity with suitable absorption and desorption kinetics at practical temperatures.

Ternary alloys based on $LaNi_5$ exhibit interesting structural and electronic characteristics, especially in the context of hydrogen storage and broader energy-related applications [1, 2]. Specific properties of the material can be systematically tuned by alloying with different elements, i.e by partial substitution of individual atoms [3]. Such modifications can significantly influence the crystal structure, lattice size and parameters, playing a critical role in hydrogen absorption properties [4].

Theoretical ab initio calculations assist significantly in the development of new materials. For example, they elucidate how the hydrogen interacts with the metal alloys [5], reveal the relationship between the atomic structure and physical properties [6 – 8] and also predict novel materials with desired characteristics that have not been experimentally realized yet. Moreover, valuable information on mechanical and thermal properties can be extracted from accurate phonon dispersion calculations [9]. Phonons, quasiparticles representing the atomic vibrations in solids, influence not only the mechanical properties of materials (e.g. structural stability), but also their thermal properties such as thermal conductivity, heat capacity and entropy.

The La-Ni-Sn system, where the Sn partially substituted Ni in the $LaNi_5$ structure, has shown promising hydrogen absorption characteristics. It was experimentally reported that Sn substitution expands the unit cell and reduces the hydrogen equilibrium pressure compared to pure $LaNi_5$, i.e. this indicates stronger hydrogen bonding to the metal matrix [10, 11], which is advantageous for hydrogen storage applications. The theoretical investigations of the La-Ni-Sn system reported so far have primarily focused on electronic structure calculations [12 – 14], while the phonon-related studies remain limited. There are some calculations of phonon band structures for pure $LaNi_5$ [15 – 17] and its partially Al-substituted modifications [18, 19]. However, no comprehensive study addresses the vibrational properties of Sn-substituted $LaNi_5$ compound.

This study is motivated by the limited theoretical understanding of the La-Ni-Sn system and its hydrides, particularly regarding phonon-related properties. We focus on one specific hydride, $H_1LaNiSn$, and employ a quantum-mechanical approach to explore its stability, equilibrium characteristics, phonon spectra, electronic structure and hydrogen absorption behavior.

2. COMPUTATIONAL METHODOLOGY

Quantum-mechanical calculations in this study were performed employing the pseudopotential method incorporated in the Vienna Ab initio Simulation Package (VASP) [20, 21] within the framework of Density Functional Theory (DFT) [22, 23]. The exchange and correlation energy was treated by the Generalized Gradient Approximation (GGA) in the parametrization of Perdew, Burke and Ernzerhof (PBE) [24] with the Projector-Augmented Wave (PAW) pseudopotentials [25, 26]. Specifically, the pseudopotentials used were: H_h, Ni_sv_GW, Sn_sv_GW and La_GW from the potpaw_PBE.64 VASP database. The plane-wave energy cut-off was set to 870 eV. The Brillouin zone sampling was defined via the KSPACING parameter set to $0.01 nm^{-1}$, corresponding to a 9×8×15 *k*-point mesh for the 16-atom unit cell. The Methfessel-Paxton smearing scheme of order 1 (ISMEAR = 1) with smearing width (parameter SIGMA) of 0.095 eV was applied for automatic complete relaxation of the 16-atom computational unit cell containing 4 atoms of H, 4 atoms of La, 4 atoms of Sn and 4 atoms of Ni, see **Figure 1(a)**, providing the equilibrium atomic positions, cell shape and volume. The phonon band structure and the phonon density of states were calculated using the Phonopy software [27]. For these calculations, a 96-atom cell, constructed as a $\sqrt{2}\times\sqrt{2}\times3$ multiple of the relaxed 16-atom cell within a rotated coordination system, was employed.

3. RESULTS

In this work, the experimental crystallographic data (lattice parameters a = 0.72601 nm, b = 0.86465 nm and c = 0.44878 nm) were used as the input for DFT calculations performed in VASP. The energy-volume (E-V) data obtained from volume relaxation were fitted using the Murnaghan equation of state (see **Figure 1(b)**) to extract key mechanical properties such as the equilibrium volume V_0, the bulk modulus B_0 and its pressure derivative B_0'. The energy minimum was identified at V_0 = 0.177175 nm^3/atom and E_0 = −5.2059 eV/atom (indicated by a triangle in **Figure 1(b)**). The fitted bulk modulus is B_0 = 84.77 GPa with a pressure derivative B_0' = 4.35.

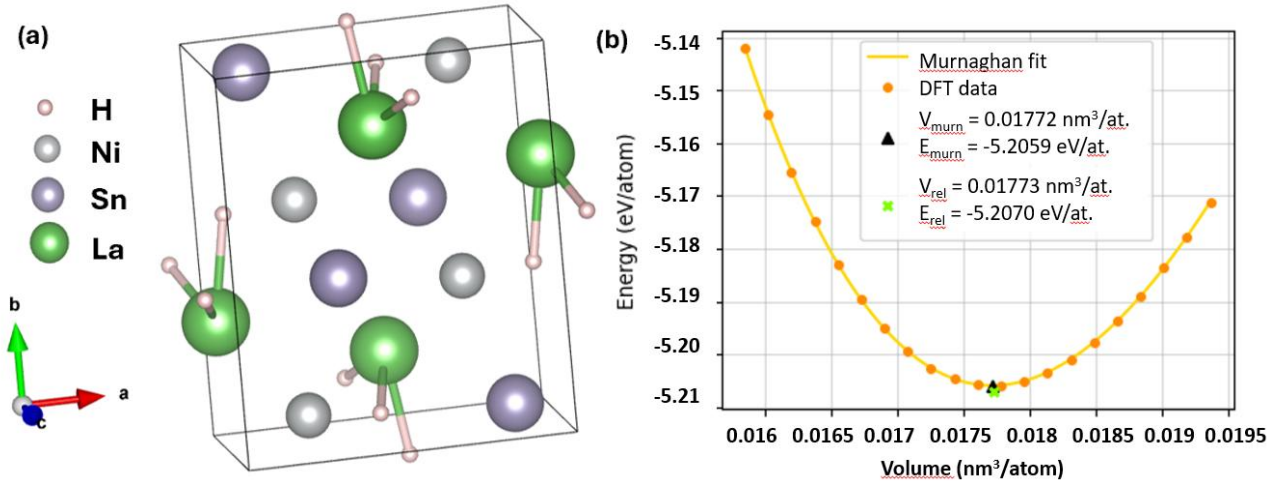

Figure 1 (a) Schematics of the 16-atom unit cell of $H_1LaNiSn$ used for VASP calculations. (b) The DFT calculated energy-volume curve of $H_1LaNiSn$ (full yellow circles) fitted by the Murnaghan equation of state (yellow curve). The full black triangle indicates the *E*-*V* curve minimum and the green cross corresponds to the position of the completely relaxed ground state

The high quality of the fit confirms the suitability of the Murnaghan equation for accurately describing the volumetric response of this system near equilibrium. The equilibrium parameters obtained after the complete relaxation (the INCAR-file tag ISIF = 3) of the 16-atom unit cell are: a = 0.73115 nm, b = 0.86992 nm and c = 0.44593 nm, equilibrium volume V_0 = 0.177269 nm^3/atom.

To investigate the vibrational properties of the $H_1LaNiSn$ system, phonon calculations were performed using DFT data implemented in the Phonopy package. The interatomic force constants derived from DFT were used to compute both the phonon band structure and the Phonon Density Of States (P-DOS) through the finite displacement method. The resulting phonon band structure is presented in **Figure 2**.

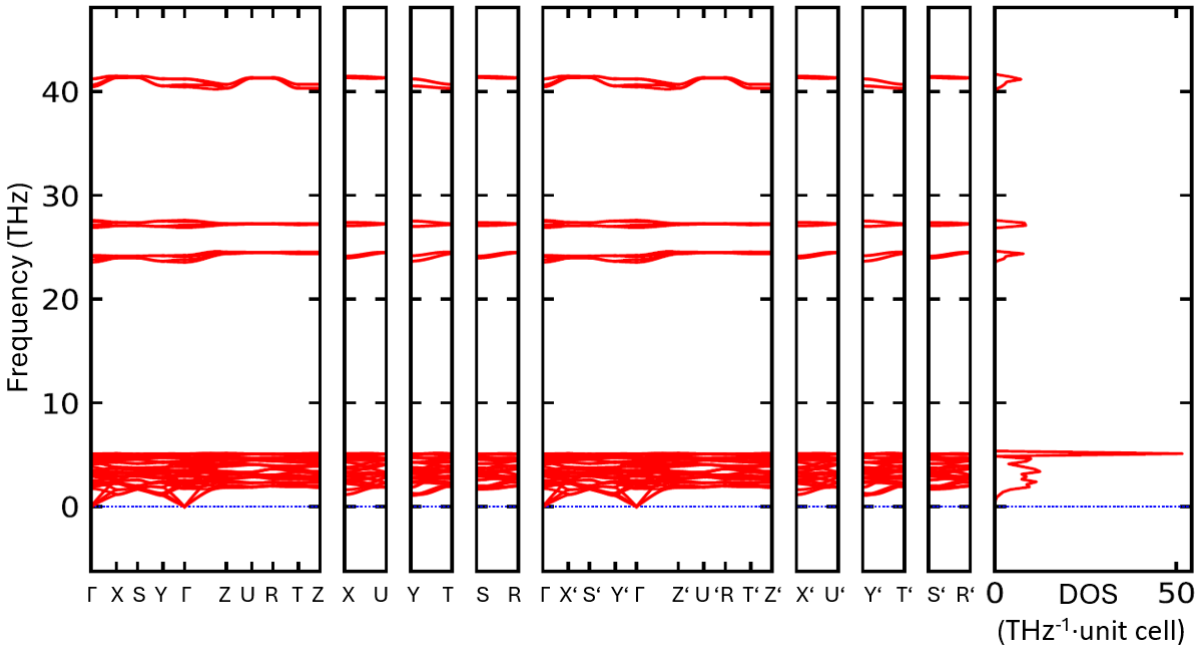

Figure 2 Phonon band structure and phonon density of states of $H_1LaNiSn$ calculated using the Phonopy package. The absence of imaginary modes confirms the dynamical stability of the structure. High-frequency flat bands suggest localized vibrations, particularly those involving hydrogen atoms

Phonon dispersion curves span the entire Brillouin zone and reveal no imaginary frequencies (no negative branches), which provides strong evidence that the H_1LaNiSn structure is dynamically stable. In phonon theory, imaginary frequencies signify structural instabilities – directions in which atomic displacements lower the system's total energy. Their absence indicates that the structure resides at a local minimum of the potential energy surface. In the optical region of the phonon spectrum, well-separated flat bands are observed at approximately 25, 28 and 41 THz. These flat bands correspond to localized vibrational modes likely associated with the lighter hydrogen atoms due to their low atomic mass and strong bond stiffness.

To complement the phonon band structure analysis, the phonon density of states shown in the rightmost part of **Figure 2** was also computed. The P-DOS reveals several distinct peaks distributed across the frequency spectrum. The low-frequency region (below approximately 10 THz) is dominated by acoustic modes and low-energy optical vibrations. Together, the phonon band structure and P-DOS provide clear evidence that the H_1LaNiSn compound is dynamically stable at zero temperature and pressure. The absence of imaginary frequencies in the band structure and only positive vibrational states through the entire Brillouin zone in the P-DOS confirm that the structure resides in a stable configuration with no instabilities.

The thermodynamic properties of the H_1LaNiSn phase were calculated using the Phonopy package. The temperature dependence of the Helmholtz free energy (F), entropy (S) and constant-volume heat capacity (C_V) was evaluated in the range from 0 to 1000 K. The resulting trends are presented in **Figure 3**. The heat capacity C_V rises with temperature and approaches the classical Dulong–Petit limit at high temperatures. This limit (approximately $3R \approx 24.94$ J/(K·mol), where R is the universal gas constant) represents the classical molar heat capacity of solids and reflects typical solid-state behavior in the harmonic approximation.

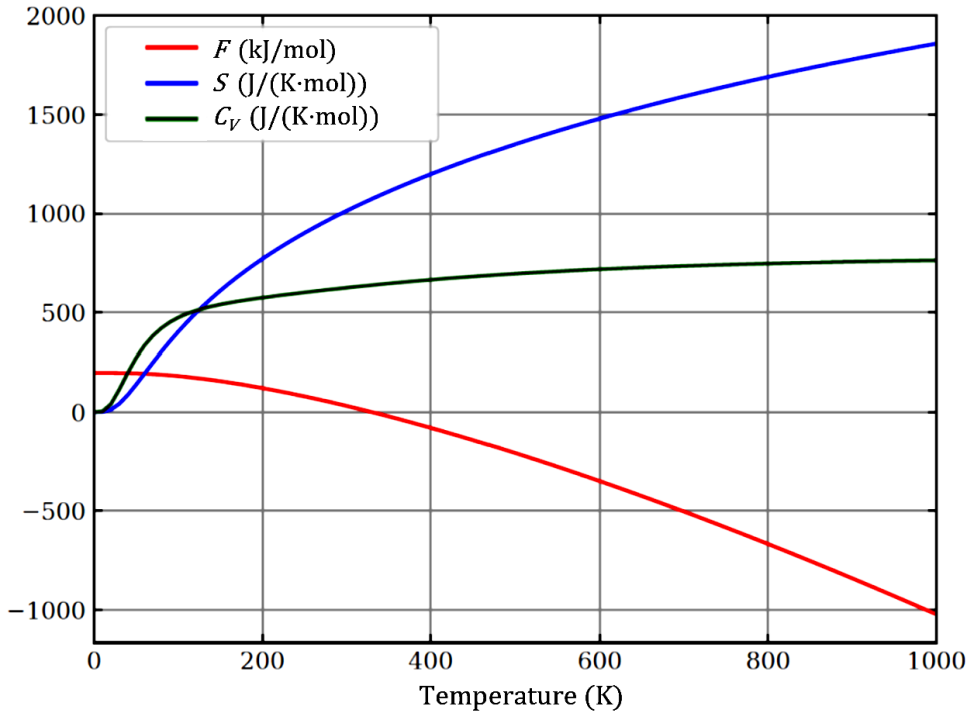

Figure 3 Computed phonon-related thermal properties of the H_1LaNiSn: Helmholtz free energy F, entropy S and constant-volume heat capacity C_V.

4. CONCLUSIONS

In this study, we conducted a detailed quantum-mechanical investigation of the $H_1LaNiSn$ intermetallic phase, focusing on its equilibrium properties and vibrational behavior, using DFT combined with the Phonopy package. The absence of imaginary frequencies in the phonon band structure confirms the dynamical stability of the $H_1LaNiSn$ structure. The phonon density of states reveals significant higher-frequency contributions from hydrogen atoms, highlighting their important role in the vibrational characteristics of the material. Overall, these findings provide valuable insights into the thermodynamic and mechanical stability of $H_1LaNiSn$, offering a theoretical foundation for future experimental and computational investigations aimed at its potential for hydrogen storage applications.

DATA AVAILABILITY

The VASP input and output files are available under DOI:10.5281/zenodo.15386551.

ACKNOWLEDGEMENTS

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