COMBINED EXPERIMENTAL AND THEORETICAL STUDY OF STABILITY OF La_2Ni_7

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Abstract

The La-Ni binary system, and in particular the $LaNi_5$ binary intermetallic phase, has been intensively studied in recent decades, especially as a promising hydrogen storage material. Knowledge of phase equilibria is very important for the possible optimization of material properties. This work is focused on the study of the thermodynamic properties of the La_2Ni_7 phase, which occurs in phase equilibrium with the $LaNi_5$ phase and can therefore influence the capacity and dynamics of these hydrogen storage materials in real materials. The alloy samples were prepared from pure elements using a gravity melting furnace in an inert Ar-6N atmosphere. The overall composition and chemical composition of the phases were analyzed by SEM-EDX. The crystal structure of the phases was confirmed by powder XRD. Our experiments were complemented by quantum-mechanical calculations implementing the density functional theory (DFT) within the generalized gradient approximation (GGA) to determine the ground-state structural, electronic, thermodynamic, and elastic properties of La_2Ni_7. A computational unit cell of La_2Ni_7 contains 36 atoms and has a strongly anisotropic shape. The computed results obtained for static lattices indicate that La_2Ni_7 is thermodynamically stable with respect to the decomposition into elemental end members. The stress-strain method was used to address the mechanical stability by computing a full tensor of the second-order elastic constants and La_2Ni_7 has been found to be mechanically stable.

Keywords: La-Ni, quantum-mechanical calculations, stability, thermodynamics, elasticity

1. INTRODUCTION

The La-Ni binary system has been intensively studied for decades for its potential use as a hydrogen storage material [1]. The hydrogen sorption and desorption properties can be effectively optimized by using a mixture of phases or by adding a third element [2]. Knowledge of phase equilibria can be advantageously used in optimizing the composition and coexistence of phases at given temperatures.

Nine phases can be found in binary system La-Ni [3]: La_3Ni (crystal structure Fe_3C, oP16-Pnma), La_7Ni_3, (structure type Fe_3Th_7, hP20-P63/mc), LaNi (structure type CrB, oS8-Cmcm), La_7Ni_{16} (structure type La_7Ni_{16}, tI46-I-42m), La_2Ni_3 (structure type La_2Ni_3, oS20-Cmca), $LaNi_3$ (structure type $PuNi_3$, hR36-R-3m), α-La_2Ni_7 (structure type Ce_2Ni_7, hP36-P63/mmc), β-La_2Ni_7 (structure type Gd_2Co_7, hR54-R-3m), La_5Ni_{19} (structure type Pr_5Co_{19} (Sm_5Co_{19}), hP48-P63/mmc), $LaNi_5$ (structure type $CaCu_6$, hP6-P6/mmm).

The La-Ni phase diagram is shown in **Figure 1**. The binary phase of $LaNi_5$ is known to form relatively stable $LaNi_5H_x$ hydrides when reacted with hydrogen. The presence of other phases can affect the thermodynamic and kinetic properties of this reaction. The stability of the closest phase La_5Ni_{19} is not clearly described in the literature. Ye et al. [4] consider it to be stable in the temperature range RT-1004.5 °C based on older experimental work.

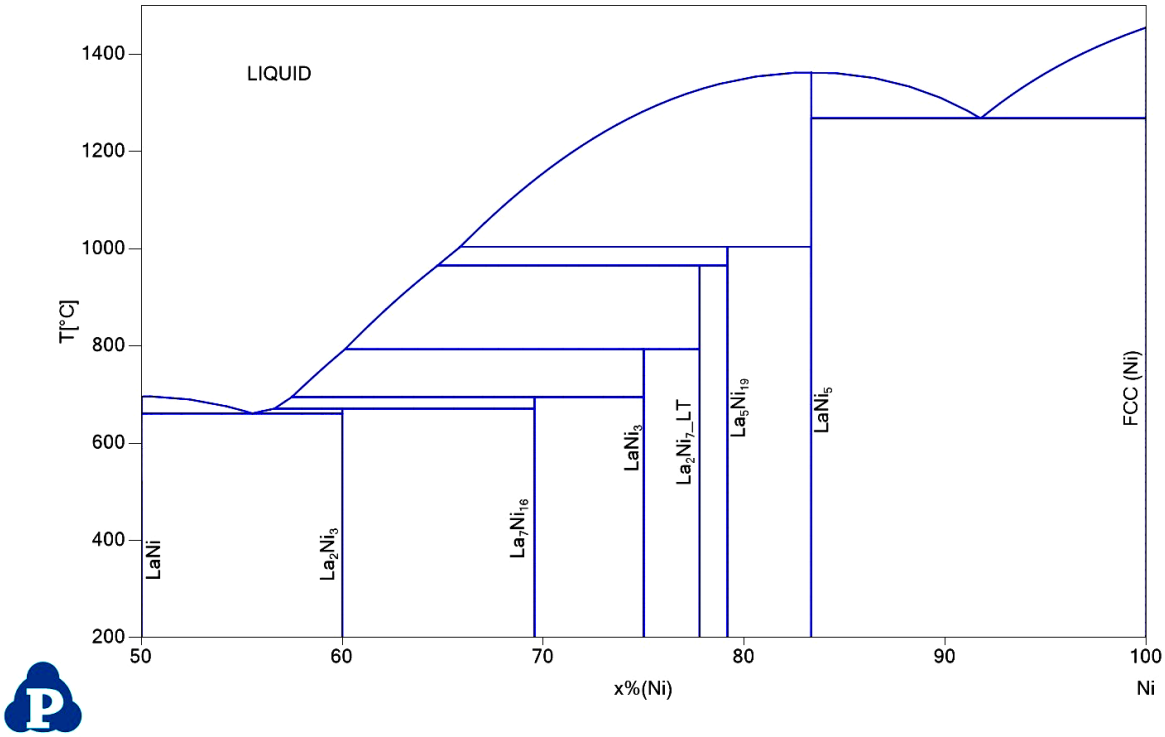

Figure 1 Phase diagram La-Ni proposed by Ye [4] includes La_5Ni_{19} binary phase

2. EXPERIMENTAL STUDY

The overall composition of the experimental sample was chosen with the main aim of describing the $LaNi_5$ phase and its surrounding. Sample as prepared from pure elements using a vacuum gravity furnace under an inert atmosphere of Ar-6N. The casted alloy with the overall composition 19.7La-80.3Ni (at.%) was analyzed and characterized by a combination of analytical methods. Overall and phase chemical composition was measured by scanning electron microscopy with energy dispersive X-ray detector (SEM-EDX). The SEM observation was performed by LYRA TESCAN microscope. Microstructure of casted sample is in **Figure 2**.

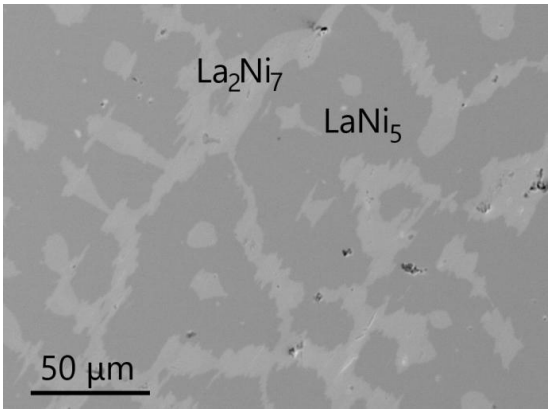

Figure 2 Microstructure of the casted sample La-Ni consisting of $LaNi_5$ and La_2Ni_7 phases in BSE mode.

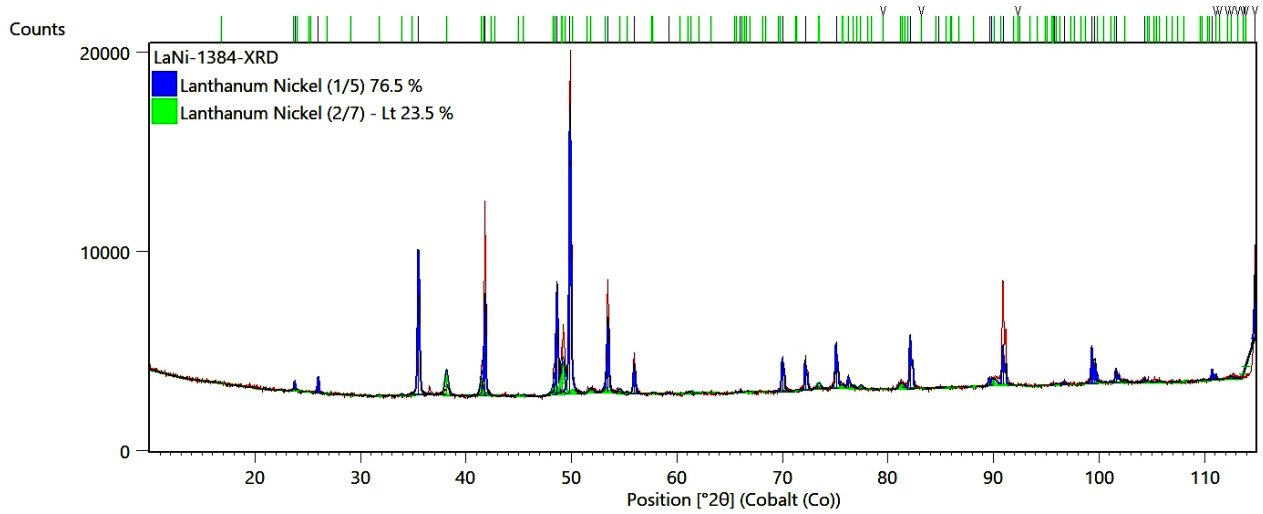

Figure 3 XRD pattern of the casted sample LaNi consisting of 76.5% $LaNi_5$ and 23.5% La_2Ni_7 phases. Measured diffractogram shown in red, calculated pattern refined with the Rietveld method for $LaNi_5$ shown in blue and La_2Ni_7 in green

The X-ray characterization of our samples was performed by the automatic diffractometer Empyrean Pananalytical (Netherlands) with Co$K\alpha_{1,2}$ radiations at room temperature. The qualitative and quantitative analysis of data was performed by HighScore 4+ (Pananalytical) program using the ICSD Database FIZ Karlsruhe (PAN ICSD, Germany) using the Rietveld model with external Si standard. Crystallographic structures of found phases were confirmed by powder X-ray diffraction (XRD) with the XRD pattern shown in **Figure 3**. The information obtained on the structure analysis of the casted samples shows that the La_2Ni_7 phase appears to be kinetically stable in coexistence with the $LaNi_5$ phase. Thermodynamic stability will be studied in future work using long-term annealed samples.

3. COMPUTATIONAL METHODOLOGY

Regarding our first-principles calculations, we employed the Vienna Ab initio Simulation package (VASP) [5,6] that implements the density functional theory (DFT) [7,8] using projector augmented waves (PAW) [9,10] (pseudo-)potentials. In particular, an 11-valence-electron La potential (core=Kr4d) and 16-valence-electron Ni_pv potential from the potpaw_PBE.52 VASP database were used. The exchange-correlation energy was parametrized within the generalized gradient approximation (GGA) by Perdew, Burke and Ernzerhof (PBE'96) [11]. The plane-wave energy cut-off was set to 520 eV. Due to the fact that the 36-atom computational unit cell of the crystal structure of La_2Ni_7 is highly shape-anisotropic (with the ratio of the hexagonal-lattice parameters *c/a* close to 5, see **Figure 4**), its reciprocal space unit cell was sampled by 10x10x2 k-points.

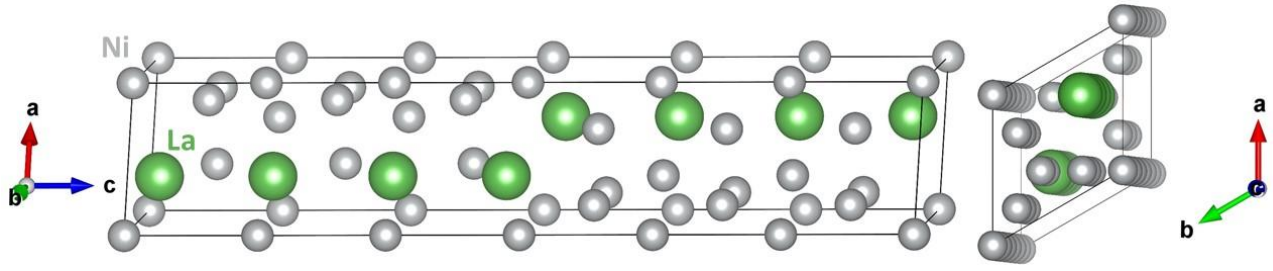

Figure 4 Schematic visualization of the 36-atom computational unit cell of crystal structure of La_2Ni_7. The computational cell 4 was visualized using the VESTA package [12].

We applied the Methfessel-Paxton smearing scheme of order 1 with the smearing parameter set to 0.05. The non-spherical contributions related to the gradient of the density in the PAW spheres were included (the LASPH parameter was set to TRUE). An additional support grid was used for the evaluation of the augmentation charges (the ADDGRID parameter was set to TRUE). Single-crystal elastic constants were computed employing the stress-strain method [13].

4. RESULTS

Our calculations started with identifying the ground-state structure of the studied La_2Ni_7 by fully relaxing the computational unit cell of La_2Ni_7 shown in **Figure 4**. The full relaxation proceeded by minimizing the energy of the static lattice with respect to the volume, cell shape as well as the atomic positions. The equilibrium lattice parameters were computed equal to *a* = 0.5023 nm and *c* = 2.4578 nm. The ground state was found magnetic with the total magnetic moment equal to 0.97 μ_B per 9-atom formula unit of La_2Ni_7 with the spin-polarization mostly associated with the Ni atoms.

In order to address the thermodynamic stability of the studied La_2Ni_7, we evaluated its formation energy ΔE_f using its mathematical expression as follows:

$$\Delta E_f(La_2Ni_7) = \frac{(E(La_2Ni_7) - 2*E(La) - 7*E(Ni))}{2+7}, \quad (1)$$

where we employed the static-lattice energy $E(La_2Ni_7)$ of the La_2Ni_7 intermetallic compound and energies of constituting pure elements in their ground-state structures. In particular, $E(La)$ stands for the non-magnetic hexagonal close-packed structure of La and $E(Ni)$ for the ferromagnetic face-centered-cubic (fcc) Ni. The computed formation energy is equal to -0.316 meV/atom. Its negative value indicates that La_2Ni_7 is stable with respect to the decomposition into elemental end members.

In order to evaluate the mechanical stability of La_2Ni_7 we determined a full-tensor of single-crystal elastic constants using the stress-strain method [12]. The elastic constants are below (in GPa) as a 6x6 matrix:

$$\begin{matrix} 191 & 110 & 83 & 0 & 0 & 0 \\ 110 & 190 & 83 & 0 & 0 & 0 \\ 83 & 83 & 207 & 0 & 0 & 0 \\ 0 & 0 & 0 & 47 & 0 & 0 \\ 0 & 0 & 0 & 0 & 47 & 0 \\ 0 & 0 & 0 & 0 & 0 & 40 \end{matrix} \quad (2)$$

The computed single-crystal elastic properties of La_2Ni_7, see eq. (2) above, are visualized in the form of directional dependences of Young's modulus and the linear compressibility in **Figure 5** employing the ELATE software [14]. As seen in **Figure 5**, the La_2Ni_7 is not strongly elastically anisotropic. Next, we also homogenized the single-crystal elastic constants according to three homogenization methods. The resulting polycrystal characteristics are in **Table 1**.

Table 1 Homogenized elastic characteristics (bulk modulus, Young's modulus, shear modulus and Poisson's ratio) according to Voigt's, Reuss' and Hill's homogenization methods as evaluated by the ELATE [14]

homogenization method	bulk modulus (GPa)	Young's modulus (GPa)	shear modulus (GPa)	Poisson's ratio (-)
Voigt	127	127	48	0.3327
Reuss	127	124	46	0.3369
Hill	127	125	47	0.3348

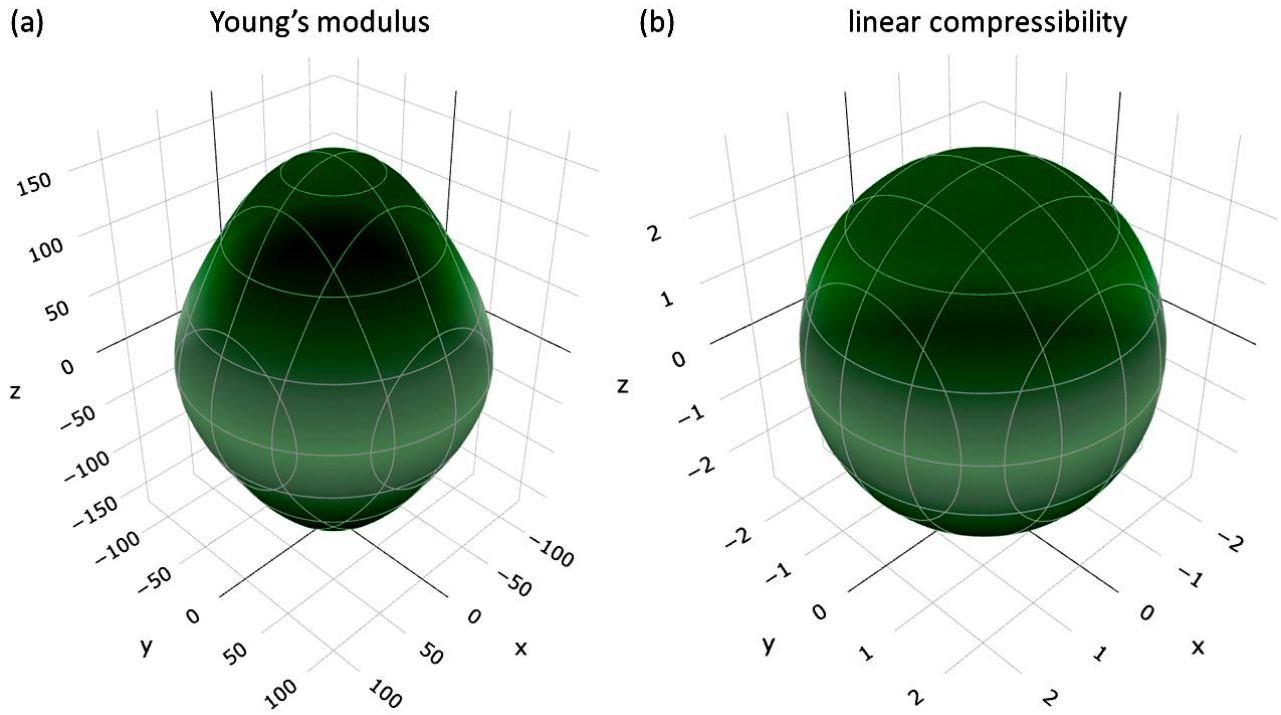

Figure 5 Directional dependences of Young's modulus (a) and the linear compressibility (b) as visualizations of the single-crystal elastic properties of La_2Ni_7. The visualization was done by the ELATE software [13] (open-access online at https://progs.coudert.name/elate)

Lastly, regarding the mechanical stability, a system is considered mechanically stable if all the eigenvalues of its 6x6 matrix of the single-crystal elastic constants are positive. We used the ELATE software to determine these eigenvalues and we got the following eigenvalues: 40, 47, 47, 80, 128, 380 (all in GPa). As they are all positive, the La_2Ni_7 is computed mechanically stable.

5. CONCLUSION

Experimental study of the casted alloys shows that the phase La_2Ni_7 is formed during quenching together with the binary phase $LaNi_5$. Existence of this phase was confirmed by SEM-EDX and XRD analytical methods. Thermodynamic stability will be analyzed from long-term annealed samples in our future research. As a complement to our experiments, we have also performed a series of quantum-mechanical calculations. The static-lattice ground-state structure of La_2Ni_7 was found by full relaxation, and its thermodynamic and mechanical stability was assessed. The formation energy of La_2Ni_7 was found negative (equal to -0.316 meV/atom) and La_2Ni_7 is, therefore, computed to be thermodynamically stable with respect to the decomposition into elemental end members La and Ni. Next, a full tensor of single-crystal elastic constants was determined using the stress-strain method. As all its eigenvalues are positive, we found La_2Ni_7 mechanically stable.

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6. SUPPLEMENTARY DATA:

The ground-state structure VASP files of La_2Ni_7 are available at DOI: 10.5281/zenodo.15387034.

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