Effect of hydrogen on stability of vacancy in LaNi₅

Masataka Mizuno 1, 2, Hideki Araki 1, 2 and Yasuharu Shirai 3

1 Center for Atomic and Molecular Technologies, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
2 Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
3 Department of Materials Science and Engineering, Graduate School of Engineering, Kyoto University, Sakyo, Kyoto 606-8501, Japan

mizuno@mat.eng.osaka-u.ac.jp

Abstract. First-principles electronic structure calculations have been performed in order to investigate the effect of hydrogen on the stability of Ni vacancy after hydrogen desorption in LaNi₅. Our calculated binding energy of hydrogen to the Ni vacancy indicates that up to two H atoms are trapped at the Ni vacancy. The formation energy of the Ni vacancy trapping H atoms was found to decrease with the number of H atoms and to turn negative when two H atoms are trapped. These results suggest that the Ni vacancy is energetically stabilized by trapping two H atoms in hydrogen desorption process.

1. Introduction

The intermetallic compound LaNi₅ possesses exceptional properties that are suitable for hydrogen storage materials. The hydrogen absorption process accompanies large volume expansions, which causes the formation of lattice defects. Our positron lifetime measurement revealed that not only dislocations but also vacancies and vacancy clusters are formed by the initial hydrogen absorption process in LaNi₅ and excess vacancies are still contained in the specimen after hydrogen desorption [1]. Furthermore, we investigated the recovery process of the excess vacancies to find that vacancy migration and annihilation are observed around 423 – 673 K [2]. This temperature range corresponds to the release temperature of residual hydrogen in the specimen after hydrogen desorption in LaNi₅ [2]. Residual hydrogen in LaNi₅ is, therefore, most likely trapped by vacancies induced by hydrogen absorption-desorption process. Calculated positron lifetimes of LaNi₅ indicate that vacancies formed by hydrogen absorption-desorption process are composed of Ni vacancies [3,4]. However, calculated formation energy of the Ni vacancy in LaNi₅ is about 1.0 eV [5], which indicates that the concentration of vacancies is 10⁻¹⁷ at ambient temperature. These results suggest that H atoms trapped at the Ni vacancy energetically stabilize the Ni vacancy.

In the present work, we examine the effect of H atoms on the stability of the Ni vacancy after hydrogen desorption in LaNi₅ using first-principles electronic structure calculations. The heats of solution of hydrogen both to interstitial sites and to the Ni vacancy are calculated in order to evaluate binding energies of hydrogen to the Ni vacancy. We also calculate formation energies of the Ni vacancy taking into account the H atoms trapped at the Ni vacancy.
2. Computational method

We employed the Vienna ab initio simulation package (VASP) [6,7] with generalized gradient approximation proposed by Perdew and Wang [8]. Potential based upon the all-electron projector augmented wave (PAW) method were used [9,10]. The intermetallic compound LaNi$_5$ crystallizes in the hexagonal CaCu$_5$ type structure, which belongs to the space group $P6/mmm$, with lattice parameters of $a = 5.0228$ Å and $c = 3.9826$ Å [11] as shown in figure 1. First, we calculated the equilibrium lattice parameters of LaNi$_5$ using the kinetic energy cutoff of 350 eV and a 15×15×19 $k$-mesh in the Monkhorst-Pack scheme with the unit cell including six atoms. We obtained the equilibrium lattice parameter of $a = 5.0107$ Å and $c = 3.9690$ Å, which well reproduces the experimental values. The structure of LaNi$_5$ consists of stacking of two types of layers: one is composed of La atoms at the 1$a$ sites and Ni atoms at the 2$c$ sites, the other is composed of Ni atoms on the 3$g$ sites.

Our results using positron lifetime measurements and theoretical calculations ruled out the possibility of the formation of La vacancies during hydrogen absorption [3,4]. In addition, in our previous work, it was found that the formation energy of the Ni vacancy at the 2$c$ site is about 0.8 eV lower than that at the 3$g$ site [5]. The Ni vacancy at the 2$c$ is, therefore, considered in the present work.

In the case of intermetallic compounds, vacancy formation process accompanies formation of other types of defects or precipitation of other phases in order to maintain the chemical composition. The formation of Ni vacancies in LaNi$_5$ proceeds via the reaction [5]:

$$0 \rightarrow V_{Ni} + \frac{1}{7}(\text{Ni}_{\text{dumbbell}} + \text{LaNi}_\text{5}).$$  \hspace{1cm} (1)

Two Ni atoms removed as vacancies occupy one La site as a Ni-Ni dumbbell along the $c$-axis. One La atom removed for the formation of a Ni-Ni dumbbell requires extra La + 5Ni sites. One Ni-Ni dumbbell, therefore, accommodates seven Ni atoms. On the basis of this process, the formation energy of Ni vacancy can be calculated as

$$\tilde{E}^{\text{Ni}}_{\text{vac}} = E^{\text{LaNi}_5}_{\text{tot}} (N_{\text{La}}, N_{\text{Ni}} - 1) - E^{\text{LaNi}_5}_{\text{tot}} (N_{\text{La}}, N_{\text{Ni}})$$

$$+ \frac{1}{7} [E^{\text{LaNi}_5}_{\text{tot}} (N_{\text{La}} - 1, N_{\text{Ni}} + 2) - E^{\text{LaNi}_5}_{\text{tot}} (N_{\text{La}}, N_{\text{Ni}})] + \frac{1}{7} E^{\text{LaNi}_5}_{\text{tot}} (1,5)$$  \hspace{1cm} (2)

The first term is the energy difference between the supercell including a Ni vacancy and the perfect supercell. The second term is the energy difference between the supercell including a Ni dumbbell and the perfect supercell. The last term is the energy of additional lattice site. In the hydrogen desorption process, Ni vacancies traps hydrogen atoms. The formation of Ni vacancy, therefore, proceeds by the reaction:

$$\frac{n}{2} H_2 \rightarrow (V_{Ni} + nH) + \frac{1}{7}(\text{Ni}_{\text{dumbbell}} + \text{LaNi}_\text{5}).$$ \hspace{1cm} (3)

The formation energy of Ni vacancy trapping hydrogen atom can be calculated as

$$\tilde{E}^{\text{Ni}}_{\text{vac}} = E^{\text{LaNi}_5}_{\text{tot}} (N_{\text{La}}, N_{\text{Ni}} - 1, N_{H}) - E^{\text{LaNi}_5}_{\text{tot}} (N_{\text{La}}, N_{\text{Ni}})$$

$$+ \frac{1}{7} [E^{\text{LaNi}_5}_{\text{tot}} (N_{\text{La}} - 1, N_{\text{Ni}} + 2) - E^{\text{LaNi}_5}_{\text{tot}} (N_{\text{La}}, N_{\text{Ni}})] + \frac{1}{7} E^{\text{LaNi}_5}_{\text{tot}} (1,5) - \frac{N_{H}}{2} E^H_2.$$  \hspace{1cm} (4)
Here \( E(N_{\text{La}}, N_{\text{Ni}} - 1, N_{\text{H}}) \) denotes the energy of a supercell with \( N_{\text{La}} + N_{\text{Ni}} - 1 \) atoms including one Ni vacancy trapping \( N_{\text{H}} \) H atoms. The last term is the total energy of hydrogen molecule.

The heat of solution of H atom to a Ni vacancy or to an interstitial site is calculated as the energy difference from the energy of H atom in hydrogen molecule:

\[
\text{Vacancy: } E^H_{\text{Sol}} = \frac{1}{N_{\text{H}}} \left\{ E_{\text{tot}}^{\text{LaNi}}(N_{\text{La}}, N_{\text{Ni}} - 1, N_{\text{H}}) - \left[ E_{\text{tot}}^{\text{LaNi}}(N_{\text{La}}, N_{\text{Ni}}) + \frac{N_{\text{H}}}{2} E^H_{\text{tot}} \right] \right\},
\]

\[
\text{Interstitial: } E^H_{\text{Sol}} = E_{\text{tot}}^{\text{LaNi}}(N_{\text{La}}, N_{\text{Ni}}, H_{\text{int}}) - \left[ E_{\text{tot}}^{\text{LaNi}}(N_{\text{La}}, N_{\text{Ni}}) + \frac{1}{2} E^H_{\text{tot}} \right].
\]

Here \( E(N_{\text{La}}, N_{\text{Ni}}, H_{\text{int}}) \) denotes the energy of a supercell with \( N_{\text{La}} + N_{\text{Ni}} \) atoms including one H atom at an interstitial site.

The binding energy of \( N_{\text{H}} \) H atoms to a Ni vacancy is defined as the energy gain when the Ni vacancy trapping \( N_{\text{H}} + 1 \) H atoms traps one H atom from an interstitial site:

\[
E^H_b = \frac{1}{N_{\text{H}}} \left[ E_{\text{tot}}^{\text{LaNi}}(N_{\text{La}}, N_{\text{Ni}} - 1, N_{\text{H}}) + E_{\text{tot}}^{\text{LaNi}}(N_{\text{La}}, N_{\text{Ni}}) \right]
- \left[ E_{\text{tot}}^{\text{LaNi}}(N_{\text{La}}, N_{\text{Ni}} - 1, N_{\text{H}} - 1) + E_{\text{tot}}^{\text{LaNi}}(N_{\text{La}}, N_{\text{Ni}}, H_{\text{int}}) \right].
\]

In the present work, we employed the 2×2×2 supercells composed of 8 La and 40 Ni lattice sites for calculating each term of the above equations. Whereas relaxations of the atomic positions and lattice parameters were allowed for the supercells including a Ni vacancy and a Ni dumbbell, the lattice parameters were fixed for the supercells including a Ni vacancy trapping H atoms.

![Crystal structure of LaNi₅](image)

Figure 1. Crystal structure of LaNi₅.

### 3. Results and discussions

#### 3.1. Stability of hydrogen at interstitial sites

Figure 2 shows local structures around interstitial sites in LaNi₅. The 3\( f \) and 12\( n \) sites are O-sites surrounded by four Ni atoms and two La atoms. The 4\( h \), 12\( o \) and 6\( m \) sites are T-sites surrounded by four Ni atoms, three Ni atoms and one La atom, and two Ni atoms and two La atoms, respectively. The calculated heats of solution of H atom to these interstitial sites are listed in table 1. The most stable site is the 12\( n \) site that is the off-center O-site surrounded by four Ni atoms and two La atoms. This result agrees with the previous work [12]. We employ the heat of solution of hydrogen at the 12\( n \) site as the energy of a H atom at the interstitial site in LaNi₅ for the calculation of binding energy of hydrogen to a Ni vacancy.
3.2. Stability of hydrogen at Ni vacancy

There are no experimental data reported for the position of H atoms trapped at a Ni vacancy in LaNi₅. We, therefore, need to determine the initial position of H atoms by considering local structures around a Ni vacancy at the 2c site. The Ni vacancy at the 2c site are surrounded by three Ni atoms at the 3g sites in the upper layer, three Ni atoms at the 2c sites and three La atoms in the same layer, and three Ni atoms at the 3g site in the lower layer. The H atoms in LaNi₅ hydride are mainly bonded to Ni atoms. Considering the arrangement of the Ni atoms around the Ni vacancy and the position of H atoms in LaNi₅ hydride, there are two possible positions for one H atom at the Ni vacancy: one is bonded to three Ni atoms at the 3g sites and the other is a bridging site between Ni 3g and Ni 2c atoms.

We calculated the heat of solution of one H atom for both configurations and obtained the heats of solution of -0.62 eV and -0.24 eV for the H atom bonded to three Ni 3g and the H atom on the bridging site, respectively. This result suggests that one or two H atoms are trapped near the three Ni 3g atoms and further H atoms occupy the bridging sites as shown in figure 3. According to this rule we configured the initial positions of up to five H atoms at the Ni 2c vacancy and calculated the heats of solution and binding energies.

Figure 2. Interstitial sites in LaNi₅.

Table 1. Heats of solution of interstitial sites in LaNi₅.

| Site  | Type     | Heats of solution (eV) |
|-------|----------|------------------------|
| 3f    | O-site   | -0.156                 |
| 12n   | O-site   | -0.162                 |
| 4h    | T-site   | 0.003                  |
| 12o   | T-site   | -0.004                 |
| 6m    | T-site   | 0.089                  |
Figure 4 (a) shows the calculated heats of solution to a Ni vacancy at the 2c site as a function of the number of trapped H atoms. The heats of solution of V-H and V-H₂ are about -0.6 eV that is about 0.5 eV lower than that of H at the interstitial site. For V-H₃, V-H₄ and V-H₅, the heat of solution increases with the number of H atoms, but still lower than that of H at the interstitial site. This is because the high-energy sites, which are the bridging sites between Ni 2c and Ni 3g atoms, are occupied V-Hₙ>2. The calculated binding energies of H atoms to a Ni vacancy at the 2c site are plotted in figure 4 (b). Negative (positive) values indicate energy gain (penalty). Whereas V-H and V-H₂ complexes gain energy by trapping H atoms, V-Hₙ>2 complexes lose energy because of the increase in the heat of solution shown in figure 4 (a). This result clearly indicates that the number of H atoms trapped at the Ni vacancy is up to two atoms.

3.3. Effect of hydrogen on the stability of Ni vacancy.
Figure 5 shows the calculated formation energies of the Ni vacancy at the 2c site as a function of the number of trapped H atoms. There is a steep drop for V-H and V-H₂ complexes and the formation energy of the Ni vacancy turns negative at V-H₂ that is the most stable vacancy-hydrogen complex as shown in figure 4. The Ni vacancy at the 2c site is, therefore, energetically stabilized by trapping two H atoms in the hydrogen desorption process.

Figure 4. Calculated solution energies (a) and binding energies (b) to a Ni vacancy at the 2c site as a function of the number of trapped H atoms.

Figure 5. Calculated formation energies of a Ni vacancy trapping H atoms at the 2c site as a function of the number of trapped H atoms.
Our recent study using positron lifetime measurement indicates that the formation of vacancies during hydrogen absorption-desorption cycling is reduced by the addition of Sn [13]. The Sn atom seems to weaken the stabilizing effect of hydrogen on the Ni vacancy. We will address this problem in the near future.

4. Conclusions
We have investigated the effect of H atoms on the stability of the Ni vacancy in LaNi5 using first-principles calculations. Up to two H atoms occupy the low-energy sites and further H atoms occupy the high-energy sites at the Ni vacancy. The heat of solution of hydrogen to the Ni vacancy begins to increase when more than two H atoms are trapped. Therefore, the binding energy of H atoms to the Ni vacancy is negative when one or two H atoms are trapped at the Ni vacancy. On the other hand, the formation energy of the Ni vacancy trapping H atoms decreases with the number of trapped H atoms and turns to negative by trapping two H atoms. These results suggest that the Ni vacancy is energetically stabilized by trapping two H atoms after hydrogen desorption in LaNi5.

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