Hydrogen quantum effects in hydride LaNi_5H_7

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Energy eigenvalues and wave functions of hydrogen atoms in hydride LaNi_5H_7 are calculated. First-principles electronic structure calculations are employed to obtain the three-dimensional potential energy structure of each hydrogen site. These quantum effects are not negligibly small in evaluation of enthalpy of formation, an important property of hydrogen storage. Including the temperature effect from hydrogen gas, experimental values are well reproduced. The excitation probability of inelastic neutron scattering is also calculated using the wave functions obtained. © 2011 American Institute of Physics. [doi:10.1063/1.3642942]

I. INTRODUCTION

The intermetallic compound LaNi_5 and its alloys exhibit a high hydrogen storage efficiency. These materials show a high capacity and a rapid absorption/desorption rate.^{1,2} Due to the low mass of the hydrogen atom, its quantum mechanical features are not negligible. The estimation of the zero point energy of a hydrogen atom and the enthalpy of formation from quantum effects are important in the evaluation of hydrogen storage materials. In our previous work, we presented first-principles calculations for electronic structures and a quantum mechanical calculation of the hydrogen atom using its potential energy obtained through the electronic structure calculation. These are powerful tools for exploring the quantum effects of light nuclei on neutron scatterings from dilute hydrogen in a solid solution of $\text{LaNi}_5\text{H}_{0.5}$.³ We also showed that some zero point vibrational effects are present at all hydrogen sites in the solid solution phase of LaNi_5H .⁴ Some sites are combined into one site due to the zero point vibration. In this study, we reveal the hydrogen-atom quantum effects in the hydride, and we clarify their role.

When hydrogen is absorbed in a metal, it occupies interstitial sites and deforms the host lattice. Due to this lattice relaxation, the total energy is decreased. In the solid solution phase, the local deformation breaks the lattice periodicity and suppresses the movement of hydrogen atoms to adjacent sites by quantum tunneling. Therefore the hydrogen atoms form self-trapped states, which are stable and localized to the sites.⁵ In the hydride phase, the periodicity is unaltered and the hydrogen vibrational modes can be explained by the optical phonon modes. However, phonon dispersion is absent, which means we can interpret the hydrogen vibration as an isolated Einstein phonon.⁵ The zero point energy obtained from these vibrational features plays an important role in the enthalpy of formation ΔH_f (of the hydride), which has to be an appropriate value in practical use.

Hydrogen should be neither so strongly absorbed nor weakly absorbed in a material intended to be used for hydrogen storage at normal temperatures and pressures. Moderate binding energies are desirable.⁶ LaNi_5 has the appropriate binding energy ($\Delta H_f \sim -31$ kJ/mol H_2).^{7–10} For deuterium, enthalpy of formation is approximately -34 kJ/mol D_2 , which suggests that the isotope effect is not negligible.^{10,11} Although first-principles calculations can give the enthalpy of formation for hydride LaNi_5H_7 with no hydrogen quantum effects,^{12–17} the zero point energy must be introduced.

In this paper, we adopt first-principles calculations to obtain the potential energy surface for the hydrogen atom at each site in hydride LaNi_5H_7 to investigate hydrogen quantum effects. We then discuss the isotope effect in evaluation of the enthalpy of formation using the obtained zero point energies. This paper is organized as follows: The calculation method is explained in Sec. II. In Sec. III, potential energy surfaces, wave functions, energy eigenvalues, and enthalpy of formation are presented with a comparison to experiments and other theories. A short summary is given in Sec. IV.

II. CALCULATIONS

For the electronic structure calculations, we employed the quantum materials simulator (QMAS),¹⁸ which is a first-principles calculation code based on density functional theory (DFT) using the projector augmented wave (PAW) method.¹⁹ The Perdew—Burke—Ernzerhof (PBE) version²⁰ of the general gradient approximation (GGA) was used for the exchange-correlation energy. Spin independent calculations were performed because LaNi_5 is a paramagnetic substance.

The primitive cell, which contains $\text{La}_2\text{Ni}_{10}\text{H}_{14}$, is used for the hydride LaNi_5H_7 calculation. The enthalpy of formation, ΔH_f is defined by

$$\Delta H_f = \frac{1}{7} [H_{\text{La}_2\text{Ni}_{10}\text{H}_{14}} - H_{\text{La}_2\text{Ni}_{10}}] - H_{\text{H}_2}, \quad (1)$$

where H is the enthalpy of the chemical composition. In this study, we shall assume that these enthalpies are total energies obtained through first-principles calculations. Therefore,

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FIG. 1. (Color online) (a) Lattice and interstitial structure of LaNi₅ ($P6/mmm$). Two unit cells are shown to display the interstitial sites. (b) Hydrogen sites contained in planes A and B for the $P6/mmm$ structure. (c) Hydrogen sites in LaNi₅H₇ for space group, $P6_3mc$. Edge atoms are added to show the periodic and polyhedron structures. In this figure, the positions of hydrogen atoms are referred by the Wyckoff positions on $P6/mmm$ instead of those on $P6_3mc$.

the enthalpy of formation given by Eq. (1) is valid at absolute zero temperature with no consideration of zero point energy. In Sec. III E, we shall discuss contributions from these factors. For the electronic structure calculations, the cutoff energy and the number of k -points in the Brillouin zone are chosen as 544 eV (40 Ry) and 144 ($6 \times 6 \times 4$), respectively. We confirmed that change in the enthalpy of formation is less than 0.4 meV when we increase the cutoff energy to 816 eV (60 Ry) or the number of k -points to 512 ($8 \times 8 \times 8$).

For pure LaNi₅ calculations, we used the lattice constants $a_0 = 5.017 \text{ \AA}$ and $c_0 = 3.943 \text{ \AA}$, which were obtained via the optimization of the LaNi₅ unit cell. These lattice constants agree well with experimentally measured values.^{21–26} To calculate total energy of the isolated hydrogen molecule, we place the two hydrogen atoms in a cubic cell with a cell length of $10 \text{ \AA}$. These total energy calculations were performed at the same cutoff energy. Therefore, error cancellation can be expected. In this study, we also calculated the zero point energy of the hydrogen molecule. The details of the calculation are given in Sec. III E.

III. RESULTS AND DISCUSSION

A. Structure

LaNi₅ has a hexagonal lattice structure (CaCu₅ structure, space group $P6/mmm$) as shown in Fig. 1 (a), and its unit cell can be characterized by the primitive vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ with $|\mathbf{a}| = |\mathbf{b}|$, $\mathbf{a} \perp \mathbf{c}$, and $\mathbf{b} \perp \mathbf{c}$. Figure 1(b) shows the hydrogen sites in LaNi₅. As shown in this figure, the sites are on two different planes. The plane spanned by $\mathbf{a} + 2\mathbf{b}$ and $\mathbf{c}$, the (11 $\bar{2}$ 0) plane, includes 6*m*, 12*o*, and 4*h*. The plane spanned by $\mathbf{a}$ and $\mathbf{c}$, the (01 $\bar{1}$ 0) plane, includes 3*f* and 6*i*. We shall refer to these planes as plane A and plane B, respectively.

The structure of the hydride LaNi₅H₇ was derived from neutron diffraction in LaNi₅D_{6.7}.^{27,28} Two different models of the chemical composition LaNi₅H₇ were proposed: $P6_3mc$ and $P31m$. Both of these models are characterized using two unit cells of LaNi₅ along the c axis and have hexagonal lattice structure. The difference in the models is the presence of a mirror plane leading to $(x, 1 - x, z)$ on the 6*c* site in the

$P6_3mc$, while $P31m$ lacks such a mirror plane. Performing full geometry optimization with these two imposed lattice structures, showed the total energy for the $P31m$ model is 2 meV lower and enthalpy of formation is 0.03 kJ/mol H₂ lower than that of $P6_3mc$. The differences in atomic positions and lattice constants are also small. In this study, we employed the $P6_3mc$ model for hydride LaNi₅H₇.

Figure 1(c) shows the structure of LaNi₅H₇ using space group $P6_3mc$ and the optimized atomic positions are summarized in Table I. Six H atoms occupy the La₂Ni₄ octahedral site of $P6_3mc$ Wyckoff position 6*c*, six H atoms occupy the La₂Ni₂ tetrahedral site of position 6*c*, and two H atoms occupy the Ni₄ tetrahedral site of position 2*b*. While these three sites are referred to Wyckoff positions of $P6_3mc$, two different sites are assigned to the same position, 6*c*. To avoid confusion and to make the correspondence to the Wyckoff positions of $P6/mmm$ clear, we shall use the corresponding Wyckoff positions of $P6/mmm$ to refer to the hydrogen interstitial sites in the hydride. Since the three sites mentioned above for LaNi₅H₇ are very close to 6*i*, 6*m*, and 4*h* of $P6/mmm$ Wyckoff positions, respectively, each hydrogen sites shown in Fig. 1(c) are called by 6*i**, 6*m**, and 4*h** in this study. The lattice constants calculated using the $P6_3mc$ space group symmetry were $a_1 = 5.363 \text{ \AA}$ and $c_1 = 8.699 \text{ \AA}$. The measured lattice constants were $a_1 = 5.409 \text{ \AA}$ and $c_1 = 8.600 \text{ \AA}$ for LaNi₅D_{6.7}.²⁷ The difference is about 1%.

To calculate the three-dimensional potential energy surface for a hydrogen atom, we shall define a Cartesian-coordinate system. Let $\mathbf{R}_H$ be the position of a hydrogen

TABLE I. Optimized atomic positions for the $P6_3mc$ model of LaNi₅H₇. The corresponding Wyckoff positions are given in the second column.

		x	y	z
La	2 <i>a</i>	0	0	0
Ni	6 <i>c</i>	0.4985	0.5015	0.2315
Ni	2 <i>b</i>	1/3	2/3	0.0161
Ni	2 <i>b</i>	1/3	2/3	0.4629
H (6 <i>i</i> *)	6 <i>c</i>	0.5055	0.4945	0.0396
H (4 <i>h</i> *)	2 <i>b</i>	1/3	2/3	0.7971
H (6 <i>m</i> *)	6 <i>c</i>	0.1495	0.8505	0.2527

atom. For the hydrogen atoms at site $6m^*$ and $4h^*$, we shall use

$$\mathbf{R}_H = X\left(\mathbf{a} + \frac{\mathbf{b}}{2}\right) + Y\frac{\mathbf{b}}{2} + Z\mathbf{c}, \quad (2)$$

with the coordinate origin at the $1a$ site of $P6/mmm$. For the hydrogen atoms at site $6i^*$, we shall use

$$\mathbf{R}_H = X\mathbf{a} + Y\left(\frac{\mathbf{a}}{6} + \frac{\mathbf{b}}{3}\right) + Z\mathbf{c}, \quad (3)$$

with the origin at the $3f$ site of $P6/mmm$. In Eqs. (2) and (3), the planes A and B correspond to the x - z plane, respectively. Note that the Cartesian coordinates are related to the fractional coordinates, (x, y, z) given in Table I, by writing the hydrogen atom positions as $\mathbf{R}_H = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$. The obtained coordinates of the hydrogen atoms on the plane A are given by $X = 0.150$, $Y = 0$, and $Z = 0.253$ for the $6m^*$ and by $X = 0.333$, $Y = 0$, and $Z = 0.797$ for the $4h^*$ site. The $6i^*$ site is not located on plane B, but it is in close proximity to this plane. Its coordinate is given by $X = 0$, $Y = 0.019$ and $Z = 0.396$. We shall discuss the potential energy surface around these sites.

B. Potential energy surface

To find hydrogen-atom quantum-mechanical features in LaNi_5H_7 , we shall use the adiabatic approximation. In our electronic structure calculations, we use the adiabatic approximation for electrons; this means the electron can adjust to the change of the nuclear positions instantaneously. In this scheme, the nuclei behave as point particles. The considerable difference in time scales between the electrons and the nuclei, which is due to the large difference in their masses, permits such an approximation. Then we shall use this approximation between the hydrogen atom and the heavy nucleus; this means the hydrogen position can adjust to the change of the nuclear state instantaneously.

In the hydride phase, there are many hydrogen atoms in each unit cell. When we consider an N -hydrogen system, it is desirable to calculate the $3N$ -dimensional potential energy

surface and solve the many particle Schrödinger equation. However, it is too computationally intense to apply such a calculation to this system. Direct overlap of individual hydrogen wave functions should be small because the hydrogen atoms are not located in the neighbor sites. Therefore only the potential surfaces for individual hydrogen atoms are needed. To obtain the hydrogen potential energy surfaces, systematic DFT calculations were performed by placing the hydrogen atoms on regular grids in the vicinity of the hydrogen minimum energy positions.

Let $\mathbf{R}_i (i = 1, \dots, N)$ be the position of i th hydrogen atom and $\mathbf{R}_i^0 (i = 1, \dots, N)$ be the minimum energy position obtained through the structure optimization. We shall denote the total energy of $\text{La}_2\text{Ni}_{10}\text{H}_{14}$ as $E_{\text{La}_2\text{Ni}_{10}\text{H}_{14}}(\mathbf{R}_1, \dots, \mathbf{R}_i, \dots, \mathbf{R}_N)$ when the i th hydrogen is located at $\mathbf{R}_i (i = 1, \dots, N)$. For this case, we chose the energy origin to be the total energy of the optimized $\text{La}_2\text{Ni}_{10}\text{H}_{14}$. When we calculate a potential energy surface for i th hydrogen atom at $\mathbf{R}_i$, i th hydrogen atom is displaced from the stable point $\mathbf{R}_i^0$ to $\mathbf{R}_i$. Therefore, the potential energy for the i th hydrogen atom is given by

$$V(\mathbf{R}_i) = E_{\text{La}_2\text{Ni}_{10}\text{H}_{14}}(\mathbf{R}_1^0, \dots, \mathbf{R}_i, \dots, \mathbf{R}_N^0) - E_{\text{La}_2\text{Ni}_{10}\text{H}_{14}}(\mathbf{R}_1^0, \dots, \mathbf{R}_i^0, \dots, \mathbf{R}_N^0). \quad (4)$$

The hydrogen atoms at the $6m^*$ and $4h^*$ sites, located at $(0.299, 0.150, 0.753)$ and $(0.667, 0.333, 0.297)$ in the fractional coordinate system (x, y, z) , respectively, are on plane A. For these sites, we used the coordinates defined by Eq. (2). The potential energies were calculated at $0.2 \leq X \leq 0.55$, $-0.2 \leq Y \leq 0.2$, and $0.6 \leq Z \leq 0.9$ for the $6m^*$ site and at $0.5 \leq X \leq 0.85$, $-0.2 \leq Y \leq 0.2$, and $0.15 \leq Z \leq 0.4$ for the $4h^*$ site. The intervals of the grids are chosen to be 0.05 (0.232 Å), 0.05 (0.134 Å), and 0.025 (0.217 Å). The hydrogen atoms at the $6i^*$ site, $(0.506, 0.011, 0.040)$, deviate by 0.0511 Å from plane B. For these hydrogen atoms, we used the Cartesian coordinates defined by Eq. (3) and calculated the potential energy at $-0.2 \leq X \leq 0.2$, $-0.6 \leq Y \leq 0.6$, and $-0.1 \leq Z \leq 0.1$ with intervals 0.05 (0.268 Å), 0.2 (0.310 Å), and 0.025 (0.217 Å), respectively.

Figure 2 shows the profiles of the calculated potential energy surface for $6i^*$, $6m^*$, and $4h^*$. In this figure, the characters, $6i^*$, $6m^*$, and $4h^*$, on the bottom plane give the classical

FIG. 2. (Color online) Profiles of calculated potential energy surfaces for the hydrogen atoms at (a) the $6i^*$ site, (b) $6m^*$ site, and (c) $4h^*$ site. In each panel, a potential minimum which vanishes in the hydride phase is denoted by a cross on the bottom plane.

hydrogen positions (minimum potential energy positions). In the $P6_3mc$ model, the potential energy surface has mirror symmetries about $X=0$ for the $6i^*$ site and about $Y=0$ for the $6m^*$ and $4h^*$ sites. For the hydrogen atoms on the $6i^*$ site in Fig. 2(a), the potential energy surface has a potential minimum point at the classical hydrogen position, while the potential energy surface at the $6i$ site for the solid solution phase has two minimum potential points.^{3,4} In this case, the potential energy surface has a step structure in the Z direction as explained latter (see Fig. 3), and its step height is 0.25 eV, which is comparable to the zero point energy of the hydrogen atom.

In Fig. 2(b), two local minima on the plane can be seen. Here the potential energy surface in the solid solution phase has three minima.⁴ The lowest one is at the $6m^*$ site and another minimum is at the LaNi_3 tetrahedral site, which corresponds to the $12o$ site in LaNi_5 . Another $12o$ site is also located on the plane near the cross ($X \simeq 0.4$ and $Z \simeq 0.65$), but there is no potential energy minimum there. The potential minimum at the $4h^*$ site also vanishes. In Fig. 2(c), the potential minimum at the $4h^*$ site can be seen. This plot includes another $4h$ interstitial site denoted by a cross. In the solid solution phase, the potential energy surface has a minimum at each of the two $4h$ sites.⁴ The structures of many hydrides of intermetallic compounds were investigated, and empirical criteria about the minimum hole size and the minimum H-H distance were obtained by Westlake.²⁹ According to the criteria, 2.1 Å is the required minimum H-H distance to occupy all the interstitial sites.²⁹ Larger H-H distance in criterion than the H-H distance of H_2 molecule (0.75 Å) may due to the two H-induced states forming a bonding and an antibonding state as Ouyang and Lee explained it from the first-principles calculations of V-H system.³⁰ The disappearance of potential minima at these sites is related to these criteria. In fact, when a hydrogen atom approaches a cross shown in Figs. 2(b) or 2(c), the distance between the nearest neighbors becomes less than 2.1 Å. Therefore the potential

energy surface is sensitive to the atomic configuration especially the hydrogen atom position. Our results suggest that these criteria are valid.

For the calculation of the hydrogen potential energy surface, we fixed both the heavy atoms and the other hydrogen atoms at their energy optimized positions. Because all the hydrogen atoms oscillate at time scales similar to the target hydrogen atom, it may not be appropriate to fix their positions. If we displace a hydrogen atom from its energy minimum position, the forces acting on the other hydrogen atoms change through the electronic structure variation. Figure 3 shows the calculated potential energy profile for the hydrogen atom located at the $6i^*$ site with and without optimizing the other hydrogen atom positions. In this figure, the hydrogen atom is trapped at $Z \simeq 0.04$. The two potential energy curves are very similar to each other. The optimization of other hydrogen atoms always results in smaller energy values. Even though the difference is pronounced in the regions far from the potential minimum, it is less than 0.05 eV. Furthermore, the typical zero point energy of hydrogen atom is 0.1 ~ 0.2 eV, and its wave function in the ground state decays exponentially with decreasing Z along $Z \simeq 0$. Therefore, the effect of the optimization of other hydrogen atom positions is negligible for low energy states.

Because there is a periodic structure in the hydride phase, hydrogen vibrations have to be treated as optical mode phonons. However, because of weak H-H correlation shown in Fig. 3, the phonon dispersion corresponding to hydrogen oscillation should be flat. In this case, the group velocity of such a phonon is quite small; this shows that hydrogen oscillations do not propagate in the crystal. Therefore our assumption of independent hydrogen atom oscillations may be valid.

C. Wave functions and energy eigenvalues

Using the potential energy surface obtained, the discretized representation of Hamiltonian matrix is constructed, which is explained in Ref. 3. To construct the Hamiltonian matrix, we used two different complete orthonormal basis sets to treat the boundary conditions. We used the plane wave solutions of the orthorhombic cell periodic boundary conditions and the wave functions of a three-dimensional infinite height potential well. In this scheme, the Hamiltonian is given by a real symmetric matrix, and the wave functions are given by real numbers. When the hydrogen atom is tightly confined in this potential, the hydrogen wave functions and their energy eigenvalues are insensitive to the choice of the boundary conditions. Conversely, we can make a judgment that the state is truly a bound state if the wave function and the eigenvalue is boundary-condition independent.

The obtained energy eigenvalues and corresponding wave functions are summarized in Table II and Fig. 4, respectively. For the ground state, $n=0$, the eigenvalue is the zero point energy for each site. For the $6i^*$ site, the potential in the Z -direction is narrower than that of the $6i$ site in the solid solution phase. Therefore, X -directional vibration state becomes easier to excite. For the hydrogen atoms at the $6m^*$ site, the wave functions cannot extend in

FIG. 3. (Color online) Neighboring hydrogen-atom-position optimization effects on the potential energy along the z axis including the potential minimum at the $6i^*$ site.

TABLE II. Calculated energy eigenvalue of a hydrogen atom in the n th state of the hydride phase for each site. (in eV).

$6i^*$		
n	H	D
0	0.166	0.112
1	0.228	0.154
2	0.275	0.183
3	0.304	0.192
$6m^*$		
n	H	D
0	0.184	0.128
1	0.231	0.169
2	0.267	0.185
$4h^*$		
n	H	D
0	0.228	0.158

the $-Z$ direction. We obtained only one bound state for the $4h^*$ site and cannot expect other bound states due to small potential barrier height. For the $6i^*$ site, we calcu-

lated the potential energy surface with the other hydrogen atom positions optimized. This resulted in a mere 1 meV reduction in energy eigenvalues for both hydrogen and deuterium.

In this study, we found the total zero point energy for seven hydrogen atoms to be 1.278 eV and 0.878 eV for hydrogen and deuterium, respectively. The phonon dispersion of LaNi_5H_7 in $P6_3mc$ structures has been previously calculated resulting in a zero point energy of 1.490 eV per formula unit.³⁶ They also performed the phonon calculation of LaNi_5 and obtained 0.176 eV per formula unit. Thus the sum of zero point energies of seven hydrogen atom can be estimated as 1.314 eV, showing good agreement with our results.

D. Inelastic neutrons scattering

The energy spectra of hydrogen vibrations can be measured by inelastic neutron scattering.⁵ In this experiment, hydrogen atoms are used instead of deuterium atoms due to its large incoherent scattering cross section. Because of the delta-function-like interaction between neutron and nucleus, the transition probability of the hydrogen from i th to f th state by the inelastic neutron scattering is proportional to the following quantity:⁵

FIG. 4. (Color online) Isovalue surface of the calculated hydrogen wave functions at each site for (a) hydrogen and (b) deuterium. The different colors represent the different signs of the wave function.

$$\left| \int d\mathbf{R} \psi_f^*(\mathbf{R}) \psi_i(\mathbf{R}) e^{i\mathbf{Q}\cdot\mathbf{R}} \right|^2 \equiv A(\mathbf{Q}), \quad (5)$$

where $\mathbf{Q}$ is the momentum transfer from the neutron to the hydrogen atom, and ψ_i and ψ_f are hydrogen wave functions of the initial and the final state, respectively. A practical value of $Q = |\mathbf{Q}|$ is $5 \sim 10 \text{ \AA}^{-1}$. Inelastic scattering experiments were performed using single crystal $\text{LaNi}_5\text{H}_{0.12}$ and excitation spectra for $\mathbf{Q} \perp c$ and $\mathbf{Q} \parallel c$ were observed.³¹ If single crystals are used in the hydride LaNi_5H_7 neutron scattering measurements, we can also obtain the direction-dependent spectra. In the following, we shall consider $\mathbf{Q} \perp c$ and $\mathbf{Q} \parallel c$ excitations.

Figure 5 shows calculated $A(\mathbf{Q})$ values for hydrogen atoms on the $6i^*$ site (Figs. 5(a) and 5(b)) and the $6m^*$ site (Figs. 5(c) and 5(d)). For $\mathbf{Q} \perp c$ case, we averaged $A(\mathbf{Q})$ along the $\mathbf{Q}$ vector on the plane spanned by $\mathbf{a}$ and $\mathbf{b}$ because the observed spectra include the contributions from equivalent sites rotated by 120° and 240° , which we cannot separate in the spectral measurement. For $\mathbf{Q} \perp c$, $1 \rightarrow 3$ (76 meV), $0 \rightarrow 1$ (62 meV), and $0 \rightarrow 3$ (138 meV) excitations on the $6i^*$ site and $1 \rightarrow 2$ (36 meV) excitation on the $6m^*$ should result in large spectral peaks, and $0 \rightarrow 1$ (47 meV) and $0 \rightarrow 2$ (83 meV) excitations on the $6m^*$ site should result in small spectral peaks. For $\mathbf{Q} \parallel c$, $0 \rightarrow 2$ (138 meV), $1 \rightarrow 2$ (36 meV), $0 \rightarrow 2$ (109 meV), and $0 \rightarrow 1$ (47 meV) excitations on the $6i^*$ site should result in large spectral peaks. When the potential energy surface of the $4h^*$ site hydrogen atoms is extended to the nearest $12o$ -like site, it is shown that the wave functions of the excited states exist at the latter site. However, excitation from the ground state is negligible at these sites due to the small overlap of the wave functions. This leads to the small intensities defined by Eq. (5).

In experiments performed at room temperature, occupation of the first excited states should be small for both $6i^*$ and $6m^*$. Thus it is difficult to observe the peaks from excitations of $n = 1$ in the spectra. Details of hydrogen occupation have been investigated by *in situ* neutron diffraction using hydride of $\text{LaNi}_{4.9}\text{Al}_{0.1}$.³² In the experiments, a small introduction of Al into LaNi_5 is used to prevent formation of lattice defects. This results in the near full occupation of the $6i^*$ sites, but the occupation of the $6m^*$ and $4h^*$ sites remains low ($0.2 \sim 0.3$ per formula unit). Furthermore, the $12o$ -like

sites have an occupancy of 0.2 per formula unit. Therefore the spectra has large peaks at 62 and 138 meV for $\mathbf{Q} \perp c$ and at 109 meV for $\mathbf{Q} \parallel c$. However, there are many small peaks from excitations at the $6m^*$ sites and the $12o$ -like sites and continuum excitation at the $4h^*$ sites. This presents difficulties in identifying the excitation modes.

In the direction-independent hydrogen vibration spectra measured for powder samples,^{22,33–35} the lowest energy peak in the spectra is located around 60–65 meV. This peak is interpreted as excitation at the La_2Ni_4 octahedral site.^{33–35} However, a broad peak between 100 and 170 meV with a shoulder around 70 meV was observed in another study. The separate vibrational peak at 423 K could not be observed.²² However, they concluded that their spectra agreed with the previous findings. Our results show that the excitation energy from $n = 0$ to 1 on the $6i^*$ site is 62 meV (Table II), which agrees well with previous findings.

In LaNi_5 hydride, the $6i$ -like site is fully occupied and other sites are partially occupied. In the $P6_3mc$ model and the $P31m$ model, the $12o$ -like site is unoccupied. However, some experimental results suggest that occupation of the $12o$ site is comparable to that of other sites.³² The broad peaks result from hydrogen occupying various sites with different potential energies. In single crystal hydride, we can excite a certain directional mode, decreasing the number of peaks in the spectra.

E. Enthalpy of formation

In the hydride phase, enthalpy of formation, ΔH_f , was experimentally measured to be $-34.8 \pm 1.8 \text{ kJ/mol H}_2$ at 298 K (Ref. 7) and separately to be $-32.1 \pm 0.1 \text{ kJ/mol H}_2$ at 285 K.⁸ In another study, the isotope effect on ΔH_f was observed to be -31.0 kJ/mol H_2 and $\Delta H_f = -34.4 \text{ kJ/mol D}_2$.¹⁰ The difference was 3.4 kJ/mol. First-principles calculations have produced a wide distribution of enthalpy of formation values. Values of -57 kJ/mol H_2 (Ref. 12), -45 kJ/mol H_2 (Ref. 13), -40 kJ/mol H_2 (Ref. 14), and $-39.41 \text{ kJ/mol H}_2$ (Ref. 16) have been obtained. Recently, values of -31.2 kJ/mol H_2 in LDA and -31.3 kJ/mol H_2 in GGA using the full-potential linearized augmented plane wave method were obtained,¹⁵ and another study obtained a value of -29.0 kJ/mol H_2 using the same method.¹⁷ The effect of finite temperature of

FIG. 5. (Color online) Calculated $A(\mathbf{Q})$. (a) and (b) for $6i^*$ site and (c) and (d) for $6m^*$ site.

phonons and hydrogen molecules is discussed by Herbst and Hector, Jr.; they obtained -36.2 kJ/mol H_2 .³⁶

From Eq. (1), we obtained $\Delta H_f = -35.16$ kJ/mol H_2 , showing agreement with experiments and recent first principles calculations. However, this ΔH_f is defined at absolute zero and does not include important factors such as zero point energies and the hydrogen gas finite temperature effect.

To evaluate the zero point energy of hydrogen molecular vibrations, DFT calculations of the inter-atomic interaction potential were performed from $0.4\text{\AA}$ to $1.5\text{\AA}$ with an interval $0.05\text{\AA}$. The total energy measured at the potential minimum is -31.738 eV (-1.1664 hartree) with a bond length of $0.751\text{\AA}$. Then we solved the one-dimensional Schrödinger equation in terms of the relative coordinate of the two nuclei and the reduced mass of the molecule. In this calculation, we omitted the centrifugal potential term. The obtained energy eigenvalues for hydrogen isotopic molecules are summarized in Table III. The binding energies both in the experiments and the variational calculations for adiabatic potentials are -4.478 eV for H_2 , -4.513 eV for HD, and -4.555 eV for D_2 .³⁷ The difference in binding energy measured from that of H_2 is -0.035 eV for HD and -0.077 eV for D_2 , which demonstrates good agreement with those in experiments and the variational calculations.

In this study, we performed the electronic structure calculations based on the PAW method using GGA. The binding energies of molecules are generally overestimated with GGA. This is also true for the hydrogen molecule. However, the small difference in binding energy between isotopes ($2 \sim 4$ meV) suggests that the potential curve in the vicinity of the bottom is well reproduced using PAW-GGA. If we employ the same code to calculate all systems in this study, we can expect a cancellation of errors in the enthalpy of formation. Therefore this procedure is a relatively simple way to calculate the energy of hydrogen.

Next we shall consider the hydrogen gas finite temperature effects on the enthalpy. In this study, we neglect thermal excitation of La and Ni in LaNi_5 and its hydride because most of the expected correction to the enthalpies should be canceled out. To estimate the magnitude of this effect, we shall assume the hydrogen gas is a diatomic ideal gas. Then, a correction to the enthalpy is $7RT/2$, and $R = 8.31\text{J/mol} \cdot \text{K}$ is the gas constant. At 298.15 K , the correction becomes 8.68 kJ/mol.

If the zero point energies and finite temperature effects are included, the enthalpies of formation are -35.29 kJ/mol H_2 and -38.56 kJ/mol D_2 . In this calculation, the ground state energy for each site is used because excitation energies are larger than thermal energy at room temperature. These results show relatively good agreement with experimental

results and calculated results by Herbst and Hector, Jr.³⁶ From these results, the isotope effect of H/D is given by 3.27 kJ/mol H_2 . This also agrees well with observed isotope effect values of H/D (3.4 kJ/mol H_2).¹⁰

The enthalpy of formation was calculated in many studies. In the most of these calculations, however, they simply defined the enthalpy of formation as a difference of total energies and both finite temperature effects and quantum effects are neglected completely. The zero point energy of H in LaNi_5H_7 is 0.367 eV (35.40 kJ/mol) per 2H and 0.277 eV (26.73 kJ/mol) for the H_2 molecule. The difference is 0.098 eV (9.46 kJ/mol), which leads to further error cancellation when the correction for the finite temperature effect, 8.68 kJ/mol, is included. Therefore previously reported calculation results agreed with experimentally obtained values entirely by coincidence.

IV. SUMMARY

In this study, the three-dimensional potential energy surfaces of hydrogen atoms in LaNi_5H_7 hydride were obtained using PAW-GGA DFT first-principles calculations of the electronic structure. In the calculated potential profiles, some of the potential minima that can be found in the solid solution phase are not present, including those of the interstitial sites. The disappearance of the potential minima is related to empirical criteria on the minimum H-H distance. The wave functions and energy eigenvalues of the hydrogen atom at the different sites were calculated. Using obtained wave functions, we predict that the directional dependence of the hydrogen excitation can be obtained using inelastic neutron scattering. We also calculated the enthalpy of formation by including the zero point energies and the correction for hydrogen gas finite temperature effects. Most of these corrections cancel each other, and therefore, the enthalpy of formation calculated from only the total energy of the electronic structures is close to the correct value of the enthalpy of formation. This is in good agreement with experimentally obtained values. The isotope effect on the enthalpy of formation also agrees well with that of experiment.

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TABLE III. Calculated energy eigenvalues for H_2 , HD, and D_2 molecules (in eV).

n	H_2	HD	D_2
0	0.277	0.240	0.196
1	0.806	0.701	0.576
2	1.306	1.141	0.941

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