Accurate heat of formation for fully hydrided LaNi$_5$ via the all-electron full-potential linearized augmented plane wave approach

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The heat of formation, $\Delta H_f$, for La$_2$Ni$_{10}$H$_{14}$, an important property for hydrogen storage, has been a major difficulty in utilizing hydrogen as a fuel or energy carrier. A solid hydrogen storage system, like metal hydrides, is reliable, simple to engineer, and much safer than the use of other phases, and so metal hydrides still attract the most attention because of their applications in a wide range of industrial fields; those associated with energy transfer and storage were proposed two decades ago, with the innovation of new heat management processes—hydride chemical heat pumps. In particular, LaNi$_5$ and its alloys have attracted great interest due to their large hydrogen capacity, moderate stability and excellent electrochemical reactivity. It is recognized that the heat of formation is the most fundamental and important quantity for hydrides—in particular, for application to hydrogen storage systems.

Experimentally, LaNi$_5$ may store up to 6.4 atoms of hydrogen per unit cell, i.e., about $5.5 \times 10^{22}$ H atom/cm$^3$. The measured heat of formation, $\Delta H_f$, at high hydrogen density for LaNi$_5$ is about $-32$ kJ/mol H$_2$. However, recent theoretical calculations could not predict the correct heat of formation for LaNi$_5$ hydrides. Tatsumi et al. studied the heat of formation of LaNi$_5$H$^+_7$ with a plane-wave basis pseudopotential method; and obtained $-45$ kJ/mol H$_2$, which is approximately 50% more negative than experiment. This has discouraged the use of first principles total energy methods in the search for novel metal hydrides. Although the experimental value for heat of formation is obtained from the hydride with a slightly lower H concentration, it is believed that $\Delta H_f$ is not significantly changed from that of full hydride because $\Delta H_f$ is nearly independent of H concentration.

Very recently, Hector et al. improved on these results by employing the well-known pseudopotential plane-wave method, and obtained $-40$ kJ/mol H$_2$ for $\Delta H_f$, leaving about a 25% disagreement with experiment. Moreover, a ferromagnetic moment of 1.33 $\mu_B$ per LaNi$_5$ was found, whereas LaNi$_5$ is known to be paramagnetic, which raised the specter of the possible failure of spin density functional theory.

To investigate these disagreements we turn to the all-electron full-potential linearized augmented plane wave (FLAPW) method, which has earned its reputation on the accuracy of its total energy calculations. In the process, we focused on the fact that the total energy of the H$_2$ molecule plays a critical role in heat of formation calculations, as

$$\Delta H_f = \frac{1}{2} [E(\text{La}_2\text{Ni}_{10}\text{H}_{14}) - 2E(\text{LaNi}_5)] - E(\text{H}_2).$$

As is well-known, the total energies of La$_2$Ni$_{10}$H$_{14}$ and LaNi$_5$ can be obtained from the total energy calculations of their unit cells, but further approximations are required to determine the total energy of H$_2$ (e.g., supercell model, film model, etc.). The remarkable feature of Eq. (1) is that a 1% error in $E_{tot}(\text{H}_2)$ will produce more than a 100% error for $\Delta H_f$, and so it is the critical quantity for precise theoretical predictions.

In this work, we employ our unique bulk/thin film FLAPW method to determine the structure and total energies for LaNi$_5$ and its full hydride—La$_2$Ni$_{10}$H$_{14}$, and in particular for the total energy of the H$_2$ molecule to calculate $\Delta H_f$ precisely. Indeed, we demonstrate that the calculated heat of formation and the geometry structure within generalized gra-

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II. METHODOLOGY

Both the local density approximation (LDA)\textsuperscript{11} and the GGA\textsuperscript{12} are employed in the calculations. Core states (up to 5s for La and 2p for Ni) are treated relativistically, whereas while valence states are treated scalar relativistically. Muffin-tin (MT) sphere radii are chosen to be 2.80 and 1.80 a.u. for La and Ni, respectively. A MT radius of 0.65 a.u. is adopted for the calculation of the H\textsubscript{2} molecule in a film model due to the short H–H bond length, and 1.0 a.u. is used for calculations on La\textsubscript{2}Ni\textsubscript{10}H\textsubscript{14}. To perform integrations in reciprocal space, we used a 4\times4\times4 mesh for LaNi\textsubscript{5} and 4\times4\times2 mesh for La\textsubscript{2}Ni\textsubscript{10}H\textsubscript{14} following the Monkhorst-Pack scheme\textsuperscript{13}—or 192 effective k points in Brillouin zone (BZ) for LaNi\textsubscript{5} and 96 k points in the BZ for La\textsubscript{2}Ni\textsubscript{10}H\textsubscript{14}, which keeps a nearly equivalent density in reciprocal space for both. When the k mesh is increased to 6\times6\times6 for LaNi\textsubscript{5}, the total energy changes within 0.5 mRy, which will only brings an error of 0.6\% to \(\Delta H_f\). In the interstitial region for LaNi\textsubscript{5} and La\textsubscript{2}Ni\textsubscript{10}H\textsubscript{14} plane waves with energy cutoffs up to 29.2 Ry for the variational bases and 262.4 Ry for the charge and potential are employed. A key quantity, the convergence with respect to the energy cutoff (\(K_{\text{max}}\)) for plane waves, will be discussed later in detail. Within the MT spheres, lattice harmonics with angular momentum \(l\) up to 12 are adopted. For the hydrogen molecule, the film version of the FLAPW method is used with an energy cutoff for wave functions up to 56.3 Ry.

III. RESULTS AND DISCUSSIONS

A. Total energy of hydrogen molecule

As mentioned previously, as the theoretical total energy of the hydrogen molecule can be decisive for obtaining the correct heat of formation, a special treatment is applied to its calculation with the FLAPW film code. Here, in addition to the spherical and interstitial regions in the bulk code, one defines a vacuum region where the wave functions are products of two-dimensional (2D) plane waves and \(z\)-dependent functions which are solutions of the one-dimensional Schrödinger equation of the \((x,y)\)-averaged potential in the vacuum region. This not only saves much computational effort, but also allows higher precision for total energy calculations of film and molecules.\textsuperscript{10}

The total energy is calculated in a 10 Å\times10 Å 2D unit cell within both LDA and GGA. Plane waves with an energy cutoff (\(K_{\text{max}}\)) up to 56.3 Ry are used as variational bases, whereas a 506.3 Ry energy cutoff (\(G_{\text{max}}\)) is used for the charge and potential; these high energy cutoffs severely limit errors to the total energy of H\textsubscript{2}. The calculated total energies for H\textsubscript{2} are -2.288 and -2.333 Ry within LDA and GGA, respectively, and change only within 0.16 mRy (or ~1\% of \(\Delta H_f\) when the unit cell size increases to 15 Å\times15 Å. Thus, we have the required precision in the calculated \(E_{\text{tot}}(H_2)\).

B. Heat of formation with experimental structure of LaNi\textsubscript{5} and La\textsubscript{2}Ni\textsubscript{10}H\textsubscript{14}

At first, the experimental coordinates of LaNi\textsubscript{5} and La\textsubscript{2}Ni\textsubscript{10}H\textsubscript{14} were employed for the heat of formation calculations. LaNi\textsubscript{5} crystallizes in the CaCu\textsubscript{5}-type structure with one formula unit per unit cell, space group of P6\textsubscript{3}m\textsubscript{m}. The stablest hydride, La\textsubscript{2}Ni\textsubscript{10}H\textsubscript{14}, has P6\textsubscript{3}mc symmetry with a doubled LaNi\textsubscript{5} unit cell along the \(c\) axis and hosts 14 hydrogen atoms. The structure of La\textsubscript{2}Ni\textsubscript{10}H\textsubscript{14} is shown in Fig. 1 with site type classifications for Ni and H. The experimental lattice parameters are \(a=5.017\) Å, \(c=3.970\) Å for LaNi\textsubscript{5} and \(a=5.409\) Å, \(c=8.600\) Å for La\textsubscript{2}Ni\textsubscript{10}H\textsubscript{14}.\textsuperscript{6}

Now, overcompleteness is a problem often encountered in total energy calculations with a high energy cutoff plane wave basis. In a usual diagonalization routine for general eigenvalue problems, the overlap matrix \(S\) is factorized by the Cholesky method assuming that the matrix \(S\) is positive definite. In some cases for an LAPW basis set, however, some eigenvalues of \(S\) could have almost zero value as there is a near linear dependence in the LAPW basis set, especially in the case of a very large energy cutoff for a plane wave basis, as in the total energy calculations in this work. For example, the total energy of LaNi\textsubscript{5} drops “anomalously” for \(K_{\text{max}}\) beyond 23 Ry which clearly shows the overcompleteness problem and causes trouble for \(\Delta H_f\) calculations. Fortunately, the canonical orthogonalization method can circumvent this problem.\textsuperscript{14} It diagonalizes the overlap matrix \(S\) and eliminates small eigenvalues less than a certain criterion (in
La$_2$Ni$_{10}$H$_{14}$ are employed. The geometry structure of LaNi$_5$ and La$_2$Ni$_{10}$H$_{14}$ was fully optimized with a plane wave basis energy cutoff ($K_{\text{max}}$) for both LDA and GGA. The experiment coordinates and lattice parameters are used for La$_2$Ni$_{10}$H$_{14}$ and LaNi$_5$. K mesh of $4 \times 4 \times 4$ for LaNi$_5$ and $4 \times 4 \times 2$ for La$_2$Ni$_{10}$H$_{14}$ are employed. The $K_{\text{max}}$’s for H$_2$ total energies are scaled according to $K_{\text{max}} \times R_{MT}=$constant.

In our case, $10^{-6}$ and their corresponding eigenvectors—namely, the (almost) linear dependent part of the LAPW basis functions.

Both LaNi$_5$ and La$_2$Ni$_{10}$H$_{14}$ were first treated nonspin polarized as they are known to be paramagnetic; their magnetic properties will be discussed later. The convergence of the total energy of La$_2$Ni$_{10}$H$_{14}$ stills goes down by more than 30 mRy when $K_{\text{max}}$ increases from 25.0 to 29.2 Ry. Here, the convergence of $\Delta H_f$ is checked with respect to increasing $K_{\text{max}}$, which is shown in Fig. 2. Noticing that different $R_{MT}$’s are adopted for H in the H$_2$ and La$_2$Ni$_{10}$H$_{14}$ calculations, the total energy of H$_2$, $E_{H_2}(K_{\text{max}})$, is converted to $E_{H_2}(K_{\text{max}}/0.65)$ in order to keep $K_{\text{max}} \times R_{MT}$ the same in both, $\Delta H_f$ converges well as it changes by less than $10^{-1}$ kJ/mol H$_2$ when $K_{\text{max}}$ increases from 25.0 to 29.2 Ry (see Fig. 2). It also shows that the GGA calculations converge slower than the LDA calculations due to the smaller localization of the exchange-correlation potential within GGA.

C. Structure optimization and formation energy

With the experimental lattice parameters and coordinates, the maximum residual force is more than 40 mRy/bohr within both LDA and GGA; thus, further relaxation is required for a more precise calculation of $\Delta H_f$. Hence, the geometry structure of LaNi$_5$ and La$_2$Ni$_{10}$H$_{14}$ was fully optimized with a $K_{\text{max}}$ of 19.4 Ry; the calculated forces show no remarkable changes when $K_{\text{max}}$ increases to 25.0 Ry and higher. This indicates that the geometry structure converges much faster than the total energy with respect to the plane wave basis energy cutoff. The optimized lattice parameters for LaNi$_5$ and La$_2$Ni$_{10}$H$_{14}$ within both LDA and GGA are listed in Table I together with the total energies and the experimental lattice parameters. There are no changes in the internal structural parameters of LaNi$_5$ since its $P6/mmm$ structure is kept during the optimization.

The optimized LaNi$_5$ lattice within LDA shrinks along the (1000) and (0100) directions by 3.0% although it changes little along $c$ in comparison with experiment. Obviously, the volume of the LaNi$_5$ unit cell is strongly underestimated (by 10.4%) within LDA. The volume of La$_2$Ni$_{10}$H$_{14}$ is also underestimated (by 4.4%) within LDA. The distance of H to the nearby Ni also shrinks in general. With the poor description of the LaNi$_5$ lattice volume, the LDA total energy of LaNi$_5$ is lower by 11.0 mRy compared with that of experimental lattice; this roughly cancels out the energy gain from relaxation for La$_2$Ni$_{10}$H$_{14}$. Surprisingly, and probably due to a cancellation of errors, the final optimized LDA results also give an excellent value for $\Delta H_f$ compared to experiment, $-31.2$ kJ/mol H$_2$.

On the other hand, the GGA results give very good lattice properties for both LaNi$_5$ and La$_2$Ni$_{10}$H$_{14}$ (c.f. Table I) that are in good agreement with a previous GGA result. Details of the GGA optimized internal positions are listed in Table II, which are also close to experiment. For example, the distance of H atoms to nearby Ni atoms changes by less than 0.02 Å in comparison with experiment except that between H1 and Ni1 (enlarged by 0.05 Å). The total energy within GGA for optimized LaNi$_5$ and La$_2$Ni$_{10}$H$_{14}$ with $K_{\text{max}}$ of 29.2 Ry are 1.6 and 38.9 mRy lower than those of the corresponding experimental structures, respectively. As a result, the formation energy for the fully relaxed structures is $-31.3$ kJ/mol H$_2$ at $T=0$ K. The thermal enthalpy contribution from H$_2$ is mostly canceled out from that of LaNi$_5$ and

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**Table I.** The FLAPW optimized lattice parameters, total energies for LaNi$_5$ and La$_2$Ni$_{10}$H$_{14}$, calculated with $K_{\text{max}}$ of 29.2 Ry, and the final heat of formation within both the LDA and GGA obtained with the calculated $E_{\text{tot}}(H_2)$ values for H$_2$ ($-2.288$ Ry with LDA and $-2.333$ Ry with GGA).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>LaNi$_5$</th>
<th>La$<em>2$Ni$</em>{10}$H$_{14}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>4.866</td>
<td>4.992</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>3.796</td>
<td>3.876</td>
</tr>
<tr>
<td>$E_{\text{tot}}$ (Ry)</td>
<td>$-32.165 7998$</td>
<td>$-32.203 8591$</td>
</tr>
<tr>
<td>$E_{\text{tot}}$ (Ry)</td>
<td>$-64.242 2152$</td>
<td>$-64.348 0522$</td>
</tr>
<tr>
<td>$\Delta H_f$ (kJ/mol H$_2$)</td>
<td>$-31.2$</td>
<td>$-31.3$</td>
</tr>
</tbody>
</table>

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**Table II.** The FLAPW optimized structural data for La$_2$Ni$_{10}$H$_{14}$ with the $P6/mmc$ symmetry within GGA.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Symmetry</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>$C_{mm}$</td>
<td>0</td>
<td>0</td>
<td>0.0259</td>
</tr>
<tr>
<td>Ni1</td>
<td>$C_{mm}$</td>
<td>1/3</td>
<td>2/3</td>
<td>0.0082</td>
</tr>
<tr>
<td>Ni2</td>
<td>$C_{mm}$</td>
<td>1/3</td>
<td>2/3</td>
<td>0.4827</td>
</tr>
<tr>
<td>Ni3</td>
<td>$C_{m}$</td>
<td>0.5003</td>
<td>0.4997</td>
<td>0.2514</td>
</tr>
<tr>
<td>H1</td>
<td>$C_{m}$</td>
<td>1/3</td>
<td>2/3</td>
<td>0.8202</td>
</tr>
<tr>
<td>H2</td>
<td>$C_{m}$</td>
<td>0.1561</td>
<td>0.8439</td>
<td>0.2849</td>
</tr>
<tr>
<td>H3</td>
<td>$C_{m}$</td>
<td>0.5052</td>
<td>0.4948</td>
<td>0.0574</td>
</tr>
</tbody>
</table>

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References:
2. References 4 and 5.
La$_2$Ni$_{10}$H$_{14}$, and it will not affect the heat of formation significantly.$^7$ Clearly, with the precise FLAPW calculation and the careful treatment of the total energy of H$_2$, the theoretical heat of formation is in excellent agreement with the experiment.$^4,5$

In the next step, spin polarization is allowed in the LaNi$_5$ and La$_2$Ni$_{10}$H$_{14}$ systems; no further optimization is found due to little force change. In apparent contrast with experiment, LaNi$_5$ is found to be ferromagnetic with a magnetic moment of 1.38 $\mu_B$ per molecule unit within GGA, and 1.34 $\mu_B$ with LDA (converged at a $k$ mesh of $8 \times 8 \times 8$). There is about 0.63 $\mu_B$ per molecule unit for La$_2$Ni$_{10}$H$_{14}$ at a $k$ mesh of $4 \times 4 \times 2$, but it disappears as the mesh increases to $6 \times 6 \times 3$ (and denser) within both LDA and GGA. This is in good agreement with the work of Hector et al.$^8$, although the magnetic properties converge more quickly on $k$ points in our work. Further self-consistent calculations with spin–orbit coupling included changes the ferromagnetic state by only a small amount. Spin polarization lowers the total energy of LaNi$_5$ by about 2.9 mRy within GGA, and 1.8 mRy within LDA and changes the final heat of formation for La$_2$Ni$_{10}$H$_{14}$ to be $-30.2$ kJ/mol H$_2$ within GGA ($-30.2$ kJ/mol H$_2$ within LDA)—still in excellent agreement with experiment. Finally, we now consider the charge density, which plays the key role in an analysis of bonding mechanisms. As is well-known, the formation, dissolution, strengthening, and weakening of chemical bonds are always characterized by charge accumulation and depletion. The bonding charge density—the difference between the self-consistent density and the superposition of atomic densities with the same atomic geometry—is plotted in Fig. 3 for both LaNi$_5$ and La$_2$Ni$_{10}$H$_{14}$. It is clear that some electrons accumulate in the interstitial region around the center Ni atom in LaNi$_5$ [Fig. 3(a)]. After the full hydride is formed, most of the accumulated charges transfer to the H atoms, and lower the Coulomb energy.

The same physics is also seen from a comparison of the density of states (DOS) between LaNi$_5$ and La$_2$Ni$_{10}$H$_{14}$ in Fig. 4: the Ni 3$d$ states are located $\sim 3$ eV below $E_F$, whereas the sharp peaks above $E_F$ are from La 4$f$, and the H 1$s$ states are between $\sim 8$ eV and $\sim 5$ eV. Clearly, the sharp peak just above $E_F$ in the LaNi$_5$ DOS (cf. the inset panel in Fig. 4) is shifted below $E_F$ due to H solution, a result of states “dropping down” to the H 1$s$ range from the Ni 3$d$ region, and stabilizing the LaNi$_5$ full hydride.

In summary, the all-electron FLAPW first-principles total energy calculations give an excellent result on the heat of formation for LaNi$_5$ full hydride; the GGA results with fully relaxed structures give $\sim 31.3$ kJ/mol H$_2$ ($\sim 30.2$ if spin polarization is considered) for the heat of formation of La$_2$Ni$_{10}$H$_{14}$, in excellent agreement with experiment. This indicates that the all-electron FLAPW method is precise enough to aid in the design of hydrogen storage materials. It also gives an accurate description for the geometry structures of LaNi$_5$, and La$_2$Ni$_{10}$H$_{14}$. The bonding charge density of LaNi$_5$, and La$_2$Ni$_{10}$H$_{14}$ indicates that the H atom in La$_2$Ni$_{10}$H$_{14}$ attracts accumulated charges in the LaNi$_5$ interstitial region and lowers the total energy of La$_2$Ni$_{10}$H$_{14}$. The striking failure of spin density functional theory to properly treat the paramagnetic state of LaNi$_5$ calls attention to the need for new theoretical developments.
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