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First-principles calculations of crystal and electronic structures and thermodynamic stabilities of La–Ni–H, La–Ni–Al–H and La–Ni–Al–Mn–H hydrogen storage compounds

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ABSTRACT

First-principles density functional theory (DFT) and lattice dynamical theory (LDT) calculations have been used to investigate the crystal and electronic structures and thermodynamic stabilities of La–Ni–H, La–Ni–Al–H and La–Ni–Al–Mn–H hydrogen storage compounds. We find that all these compounds studied are dynamically stable. For LaNi_{3.8}Al_{1.2–x}Mn_xH (x = 0.2, 0.4, 0.6) hydrides, Al only substitutes Ni at 3g0 site, H occupies 12n tetrahedral site. The structural optimizations indicate that Mn prefers to substitute Ni at 3g1 site. Mn substitutions for Ni and Al decrease their stabilities. A detailed analysis of bonding interactions reveals that the covalent bonds of H with one Ni or Mn at 3g1 site and two Ni at 2c site are mainly responsible for the stabilities of these compounds. We also present a comprehensive investigation of phonon spectra and vibrational thermodynamics of LaNi_{5–x}Al_xH (x = 0, 0.25, 0.5, 0.75 and 1) and LaNi_{3.8}Al_{1.2–x}Mn_xH (x = 0.2, 0.4 and 0.6). We find that all phonon vibrations have contribution to their vibrational enthalpies; in contrast, the low-frequency phonon vibrations mainly dominate their vibrational entropies. The calculated accuracy of low-frequency phonon vibrations is closely related to crystal symmetry, supercell size and atomic distribution in selected supercell. Generally, calculated enthalpies are more accurate than calculated entropies with respect to their experimental values. We present in the current research a first-principles method to predict the variation of enthalpy with hydrogen content at hydrogenation or dehydrogenation plateau and then to identify the so-called plateau enthalpy of each La–Ni based hydrogen storage alloy. By using this method, we find that the partial substitutions of Ni by Al decrease the so-called plateau enthalpy but impair the hydrogen storage capacity obviously, while Mn and Al substitutions for Ni not only decrease the so-called plateau enthalpy but also extend the plateau length.

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Introduction

Tritium is a kind of isotope of hydrogen [1] and has similar performances with hydrogen. It has many important applications, especially in the nuclear industry. As is known, the tritium is naturally radioactive and decay into helium [2,3]. Thus, tritium storage materials need to meet some special requirements, such as low equilibrium pressure, high absorption capacity and strong ability of helium preservation. Besides, their poison resistance and lifetime are always considered. Tritium is commonly stored in uranium (U), titanium (Ti) [4–6], zirconium (Zr) [7] and the AB₅ type alloy, i.e. LaNi₅.

The intermetallic compound LaNi₅ is a promising tritium storage material [8,9]. It can not only absorb and release large amounts of tritium rapidly and reversibly, but also retain ³He produced by radioactive decay. Nevertheless, LaNi₅ cannot satisfy practical applications because it has high tritium dissociation pressure at room temperature and pulverizes easily. Partial substitutions of Ni in LaNi₅ by third elements are commonly applied to improve its tritium storage characteristics.

LaNi₅ crystallizes in the hexagonal CaCu₅ structure [10]; La atoms occupy 1a sites while two types of Ni atoms are located, respectively at 2c and 3g sites. Some previous experiments in La–Ni–Al–H have shown that the partial substitution of Ni by Al can decrease the plateau pressure of hydride, but impair the hydrogen storage capacity obviously [11,12], while Mn substitutions in La–Ni–Al–Mn–H can decrease the plateau pressure of hydrides without reducing the hydrogen content although the hysteresis factor is slightly increased [13]. Neutron diffraction [14,15] in these compounds has revealed that Al only substitutes Ni at 3g site while Mn atoms can replace Ni atoms at 2c and 3g sites. R.J. Zhang et al. [16] have performed the first-principle calculations for LaNi₄AlH and found that H atoms only occupy 12n interstitial sites which are far away from Al atoms and the covalent interactions between H and Ni determine its stability. Ch.Y. Zhang et al. [17] have also reported that Ni 3d and Mn 3d bands are the main influencing factors on the stability of LaNi₄Mn alloy. At the basis of this work, S.L. Li et al. [18] have experimentally studied further partial replacements of Ni by Cu, Fe, Cr and Mn and pointed out that LaNi_{3.8}AlMn_{0.2} alloy has lower plateau pressure and higher hydrogen storage capacity than other La–Ni based alloys. In order to reveal the effects of Mn substitutions for Ni and Al on hydrogen storage properties of these alloys, S.L. Li et al. [19] have measured the plateau pressure and hydrogen storage capacity and found that they increase with Mn content in LaNi_{3.8}Al_{1.2–x}Mn_x (x = 0.2, 0.4, 0.6) alloys. However, there is a lack of systematically theoretical analysis for the effects of Mn substitutions for Ni and Al on crystal structures and thermodynamic properties of LaNi_{3.8}Al_{1.2–x}Mn_x alloys.

Plateau pressure is an important property to evaluate hydrogen storage ability of hydrogen storage materials [20,21], but it is difficult to measure experimentally the tritium plateau pressure because tritium is rare in nature and controlled strictly as nuclear raw material. Therefore, predicting theoretically the tritium plateau pressure will be

enormously helpful for producing this kind of hydrogen storage materials. In this paper, we present a first-principles method to theoretically predict the so-called plateau enthalpies of La–Ni based hydrogen storage alloys at a given temperature.

Computational method

In this paper, we consider a situation where the storage materials M (La–Ni based alloys) can exchange hydrogen molecules with a gas-phase reservoir of hydrogen at a given chemical potential, $\mu_{\text{H}_2}(P, T)$, determined by the temperature, T, and pressure, P [22]. The grand-canonical Gibbs free energy change in hydrogen absorbed or released process is given by the following expression:

$$\Delta G = G_{M-H}(T) - G_M(T) - \frac{1}{2}\mu_{\text{H}_2}(P, T)n_H \quad (1)$$

where $G_{M-H}(T)$ and $G_M(T)$ are the Gibbs free energies for the hydrides M–H (La–Ni based hydrogen storage compounds) and M, n_H is the number of hydrogen atoms released or absorbed at temperature T. We have calculated Equation (1) starting from $T = 0$ K, $\mu_{\text{H}_2}(P, 0)$ is given by the total energy of an isolate H₂ molecule at $T = 0$ K. $G_{M-H}(T)$ and $G_M(T)$ are equal to the total energies E_{M-H}^{total} and E_M^{total} of M–H and M, which have performed using the plane-wave ultra-soft pseudopotential (PW-USPP) method based on the density functional theory (DFT) as implemented in the Castep code [23,24]. The structure optimizations of atomic positions and cell volumes of M and M–H have been carried out by means of the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm. They will stop until the total energies are converged to 10^{-5} eV/atom, the forces on each unconstrained atom are smaller than 0.03 eV/Å, the stresses are lower than 0.05 GPa and the displacements are less than 0.001 Å. The plane-wave cutoff, E_{cut} , is chosen to 300 eV. In structure optimizations, the total energy calculations with the local density approximation (LDA), the PBE, RPBE and PW91 forms of the generalized gradient approximation (GGA) as the exchange-correlation potentials [25] have been completed to estimate the loss in accuracy due to their local approximate treatments. In these calculated lattice parameters and cell volumes, the deviation from the experimental parameters and volumes is smallest for the optimized structures obtained by using the PW91 form of GGA. In order to make the k-point spacing smaller than 0.04 \AA^{-1} , the k-point meshes of $6 \times 6 \times 6$ and $6 \times 5 \times 6$ are used over the Brillouin zone (BZ) for LaNi_{3.8}Al_{1.2–x}Mn_x and LaNi_{3.8}Al_{1.2–x}Mn_xH, respectively.

To obtain $G_{M-H}(T) = H_{M-H}(T) - TS_{M-H}(T)$ and $G_M(T) = H_M(T) - TS_M(T)$, where $H_{M-H}(T)$, $H_M(T)$, $S_{M-H}(T)$ and $S_M(T)$ are the total enthalpies and entropies at temperature T, the frozen phonon method is used for performing phonon calculations within the harmonic approximation based on the density functional perturbation theory (DFPT) to determine normal mode frequencies of the ionic La, Ni, Al, Mn and H vibrations.

To demonstrate the relationship of formation energies with average bond order (BO_{H-A}), average bond lengths (BL_{H-A}) between metallic ion A (Ni, Mn, La or Al) and H and with

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