

Relationship between compressibility and hydrogen absorption in some Haucke compounds

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Abstract

In this paper, we present the results of ab-initio band structure calculations based on the local approximation of the density functional theory for several hydrogen absorbing AB₅ compounds YNi₅, LaNi₅, LaCu₅, and some substituted compounds such as LaNi_{4.5}Al_{0.5}, LaNi₄Al, LaNi₄Cu, LaNi_{4.5}Si_{0.5}, LaNi_{4.5}Ge_{0.5}, and LaNi_{4.5}Sn_{0.5}. The calculated bulk moduli obtained by total energy minimizations are in satisfactory agreement with available experimental data. These results are used, in conjunction with electronic features such as band filling and Fermi energy characteristics, to discuss the relationship between compressibilities, electronic structure and H-absorption properties in Haucke compounds.

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1. Introduction

Since in Haucke AB₅ compounds as well as in most H-absorbing transition metals and intermetallic compounds (IMC), the hydrogen absorption is accompanied by a large volume increase, the compressibility of the matrix is expected to play an important role. The elastic energy spent in the lattice expansion and the energy gained from the chemical metal–hydrogen interaction are indeed the antagonist key factors that control the stability of the hydrides. While the latter is of pure electronic origin, the former involves electronic as well as lattice properties. Substitutions at the A or B sites by elements of different sizes and (or) chemical nature are expected to affect both the electronic and elastic properties of the IMCs and consequently their hydrogen absorption properties. Experimentally, substitutions have been widely used to modulate the thermodynamic properties of hydrogen absorbing IMCs, and modify two parameters crucial for the applications of these materials, namely the plateau pressure of the hydrogen desorption isotherms and

the maximum hydrogen absorption capacity [1,2]. Empirical correlations have been established between the value of the plateau pressure of the isotherms, p_{H_2} , and (i) the unit cell volume [3,4] and (ii) the compressibility of the lattice estimated from measurements of the Debye temperature [3,5,6]. These experimental results indicate that the plateau pressure of the isotherms, p_{H_2} , decreases with increasing unit cell volume of the IMC, and with increasing value of the compressibility. However, considering the approximations on which the estimates of the compressibility rely, these correlations need further investigations. In very recent years, an increasing number of measurements by ultrasonic techniques of the elastic properties of hydrogen absorbing Laves phase [7] as well as substituted Haucke compounds became available [8,9] while theoretical calculations remain very scarce [10].

In this paper, we present the results of a systematic investigation, by means of ab-initio band structure calculations, of the electronic structure and bulk moduli of a series of Haucke compounds YNi₅, LaNi₅, LaCu₅, and some substituted alloys LaNi_{5-x}M_x (M = Al and $x = 0.5, 1.0$; M = Si, Ge, Sn and $x = 0.5$; M = Cu and $x = 1.0$). The most salient features of the electronic and elastic properties are discussed in relation

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with experimental data and hydrogen absorption properties of these materials.

2. Computational method

The electronic structure calculations have been performed using the local density approximation of the density functional theory within the linear muffin-tin orbitals method and the atomic sphere approximation [11]. The exchange and correlation term of the crystal potential was calculated using the von Barth–Hedin [12] approach and the combined correction terms were included to account for the overlap of atomic spheres. The densities of states were obtained with the linear energy tetrahedron method in a mesh of 1 mRy.

In the hexagonal Haucke compound LaNi_5 (space group $P6/mmm$), the Ni atoms occupy two types of sites, the (2c) basal plane and the (3g) middle plane sites. In the substituted compounds $\text{LaNi}_{5-x}\text{M}_x$, the M elements were substituted at the Ni (3g) sites since structural data show that for the M elements and range of x values under consideration, the substitutions occur predominantly in the (3g) rather than in the (2c) sites leading to supercells containing 12 atoms for $x = 0.5$. The effects of substitutional disorder were ignored in this work. The experimental structural data used in the present work are taken from Refs. [13–20].

We used at least 450 k points in the irreducible Brillouin zone and 150 self-consistent cycles to obtain total energies converged at least up to 10^{-5} Ry. For each of the IMC, the total energies were calculated for 10–15 different values of the unit cell volume around the experimental one. The Mur-nagham equation of state was then used to obtain the bulk moduli.

3. Results and discussion

3.1. Electronic structure

The occupied valence band of YNi_5 is very similar to that of the isovalent compound LaNi_5 [21,22] as shown in the densities of states plotted in Fig. 1. It is essentially composed of Ni-3d states hybridized with Y-4d states and with metal s-p states. The Ni-3d bands are not entirely filled and the Fermi energy falls below the valley that separates the bonding Ni–Y from the antibonding Y–Ni states, in a region of high density of Ni states, in agreement with low temperature electronic specific heat and magnetic susceptibility data [21]. As previously discussed for LaNi_5 [21,22], these intermetallics cannot be considered as charge transfer compounds in agreement with photoemission data [21]. The essential differences between the DOSs of YNi_5 and LaNi_5 are the presence of empty 4f states in LaNi_5 forming a narrow peak at 3 eV above E_F , and a slightly smaller width of the occupied Ni states associated to a larger unit cell volume.

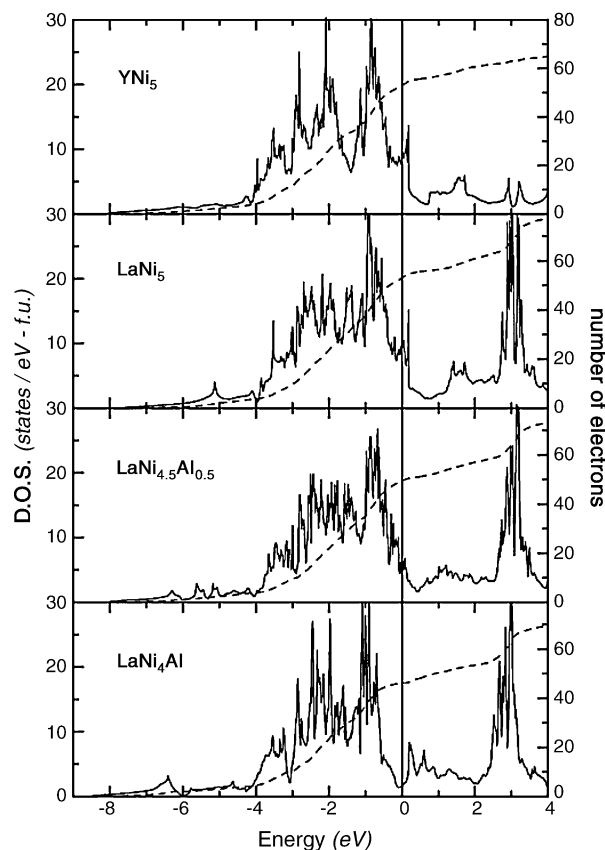


Fig. 1. Total density of states (full line, left hand side scale) and number of electrons (dashed line, right hand side scale) of YNi_5 , LaNi_5 , $\text{LaNi}_{4.5}\text{Al}_{0.5}$, and LaNi_4Al . The Fermi energy is chosen as the origin of energies.

The DOSs of $\text{LaNi}_{5-x}\text{Al}_x$ ($x = 0.5$ and 1.0) represented in Fig. 1 show that as x increases, the contributions of the Al-s states located between -8 and -4 eV, and of the Al-p states located at higher energies increase; the filling of the Ni-d states increases and the DOS at E_F decreases, in good agreement with the experimental trend obtained by Chung et al. [6] from electronic specific heat data. In LaNi_4Al , the Fermi level falls in a deep of the DOS separating the filled Ni-3d from the empty La-5d states suggesting that further increase in the substitution rate would lead to an increase of $N(E_F)$, as observed experimentally [6].

In the group IV substituted compounds $\text{LaNi}_{5-x}\text{M}_x$ ($M = \text{Si}, \text{Ge}, \text{Sn}, x = 0.5$), in contrast to the Al substituted alloys, the M-s states form distinct structures in the DOS below -8 eV, as shown in Fig. 2 while the M-p states are hybridized with the nickel and La occupied states. The Ni substitution by these isovalent s-p elements lead to a progressive filling of the Ni-d peak and to a decrease of $N(E_F)$. The Fermi level characteristics appear to be more sensitive to the substitution rate than to the chemical nature of the isovalent substituting elements [23].

In the Al and Sn substituted hydrides, the progressive filling of the Ni-d bands as a function of increasing values of x can be correlated to the observed decrease in the maximum hydrogen absorption capacity.

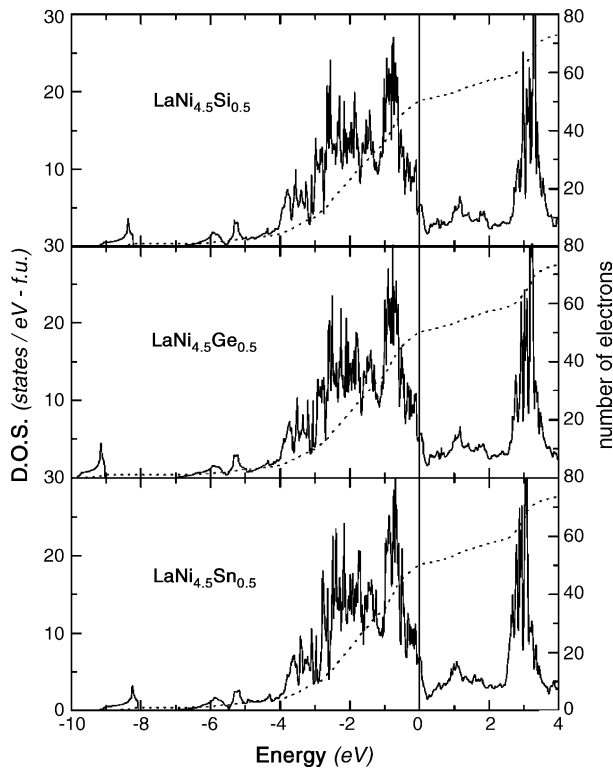


Fig. 2. Total density of states (full line, left hand side scale) and number of electrons (dashed line, right hand side scale) of group IV substituted compounds $\text{LaNi}_{4.5}\text{M}_{0.5}$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$). The Fermi energy is chosen as the origin of energies.

The DOSs of the compounds substituted at the Ni site by Cu, an s element of the 3d series, are plotted in Fig. 3. In the DOS of LaNi_4Cu , a new structure associated to the 3d states of Cu centered around -3.5 eV appears below the Fermi energy, and grows in intensity as the substitution rate increases. Concomitantly, a progressive filling of the Ni-d peak by the Cu-s electrons and a decrease of $N(E_F)$ are observed. In LaNi_4Cu , the Ni-d states are not entirely filled while in LaCu_5 , the Fermi energy falls at 1.8 eV above the filled narrow Cu-d bands, in the La-5d states. The calculated position of the additional Cu-d subband as well as the progressive filling of the Ni-d states and decreasing value of $N(E_F)$ with increasing Cu content is in agreement with photoemission data [24,25]. In contrast, we have shown that the Ni substitution by a 3d element on its left in the periodic table such as $\text{M} = \text{Mn}, \text{Fe}, \text{Co}$, leads to a new M-3d structure centered above the Ni-3d peak and to an increase of $N(E_F)$ since the Fermi energy is located in the narrow additional M-3d subbands. The increase of $N(E_F)$ leads to a tendency towards magnetic ordering as x increases.

In Fig. 4, the calculated unenhanced values of the electronic specific heat coefficient obtained from the bare DOSs at the Fermi energy are plotted against the available experimental data. The general trends are found to be in good agreement.

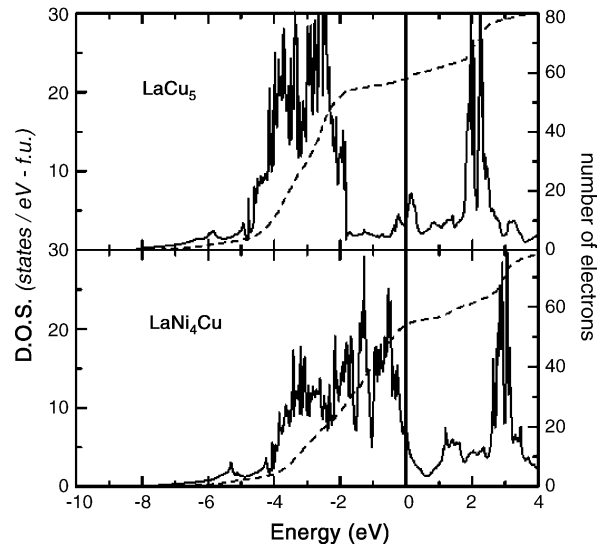


Fig. 3. Total density of states (full line, left hand side scale) and number of electrons (dashed line, right hand side scale) of LaNi_4Cu and LaCu_5 . The Fermi energy is chosen as the origin of energies.

3.2. Elastic properties

Using the calculated well converged total energies, the bulk moduli in GPa derived from the Murnaghan equation of state are listed in Table 1. They are found to be in satisfactory agreement with available experimental data on polycrystalline $\text{LaNi}_{5-x}\text{M}_x$ ($\text{M} = \text{Al}$ and $0 < x < 1$; $\text{M} = \text{Sn}$ and $0 < x < 0.5$) obtained recently with resonant ultrasound spectroscopy and ultrasonic pulse-echo techniques [8,9] as well as with data on polycrystalline and single crystals of LaNi_5 [26,27]. In the substituted Haucke compounds, the general trend observed indicates a decrease of the elastic moduli with increasing values of x .

Using the Debye temperatures obtained from their low temperature heat capacity measurements, in conjunction with

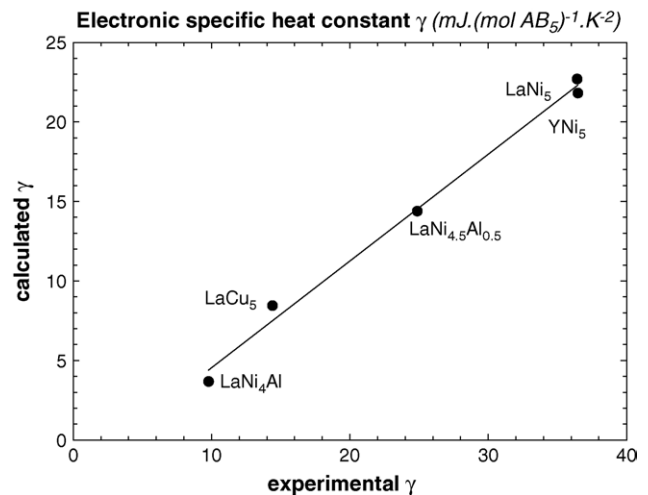


Fig. 4. Calculated unenhanced electronic specific heat coefficient γ vs. experimental data [5,6].

Table 1
Calculated and measured bulk moduli (GPa)

	B^{cal} (GPa)	B^{exp} (GPa)
YNi ₅	163	
LaNi ₅	149, 135 ^a	139 ^b , 137.4 ^c , 135.2 ^d
LaNi ₄ Cu	139	
LaCu ₅	114	
LaNi _{4.5} Al _{0.5}	137	127.8 ^c
LaNi ₄ Al	130	126.6 ^c
LaNi _{4.5} Si _{0.5}	143	
LaNi _{4.5} Ge _{0.5}	142	
LaNi _{4.5} Sn _{0.5}	123	129.8 ^d

^a Ref. [10]. ^b Ref. [26]. ^c Ref. [8]. ^d Ref. [9].

the relation derived by Madelung within the Debye theory, Takeshita et al. [3,5] estimated the relative compressibilities of several Haucke compounds. Their results provide a general trend rather than absolute values, they point out to an increase of the hydride stability with a decreasing lattice rigidity. In the present calculation, the most rigid of the IMC investigated is YNi₅, in agreement with Takeshita et al. [3,5].

We find that when Ni is substituted by a given s or s–p element, the rigidity of the lattice decreases when the substitution rate, x , increases. This result is in agreement with the trend observed from ultrasonic measurements on the Al and Sn substituted alloys [8,9]. Since the substitutions considered in our work lead to a lattice expansion, the calculated decrease of the bulk moduli is also associated to lattice expansion effects.

In Fig. 5, we plotted the experimental values of the isotherms plateau pressures, p_{H_2} , versus the calculated values of the bulk moduli. From this plot, a correlation can be established between the stability of the hydrides and the rigidity of the material. YNi₅ is by far the least compressible material and has the highest plateau pressure. For each family of substituted compounds, the straight lines in Fig. 5 are just guide lines to the eye indicating the general trend between the stability of the hydride, associated to a decrease of p_{H_2} , and the bulk modulus of the IMC. Fig. 5 shows clearly that

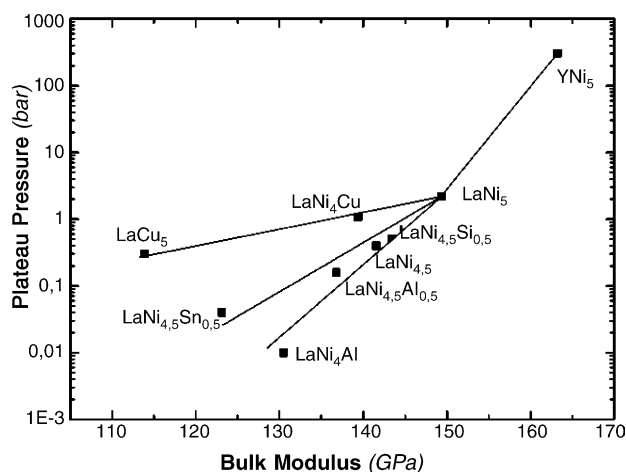


Fig. 5. Experimental values of the isotherms plateau pressures vs. the calculated bulk moduli for all IMCs investigated in this work.

in each family, the most compressible materials correspond to the most stable hydrides.

4. Summary and conclusions

In agreement with available electronic specific heat data, we find that the substitutions of Ni by s–p elements of groups III and IV lead to a decrease of the values of the densities of states at the Fermi level, $N(E_F)$. For a given substituting element, $N(E_F)$ decreases with increasing values of the substitution rate x . This decrease of $N(E_F)$ is associated to the progressive filling of the Ni-d bands and is correlated to the decrease in the maximum hydrogen absorption capacity of the intermetallic compound. When Ni is substituted by Cu, an additional subband associated to the Cu-d states develops below the Ni-d structure of the DOS, its intensity increases with increasing values of x , in agreement with photoemission data. As in the case of substitutions by s–p elements, the s electrons of Cu contribute to a progressive filling of the Ni-d bands, and thus to a decrease in $N(E_F)$. This behaviour is very different from the results obtained in our previous work by substitutions of Ni by transition elements located on its left of the periodic table (Mn, Fe, Co).

The calculated bulk moduli are found to be in satisfactory agreement with the available experimental data. We find YNi₅ to be the most rigid of the IMCs under investigation. In each family of substituted LaNi_{5-x}M_x compounds, we show that the rigidity decreases when the substitution rate by a dilating element increases, a result in agreement with the experimentally observed trends. Using experimental values of the plateau pressures of the hydrogen desorption isotherms, p_{H_2} , we have established a systematic correlation between the calculated rigidity of the ICMS and the values of p_{H_2} , that are of paramount importance for the applications of hydrogen storage materials. In each family of substituted compounds, the most compressible ICMS lead to the most stable hydrides.

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