Vol 16 No 7, July 2007
1009-1963/2007/16(07)/2056-06

Chinese Physics

Density functional theory study on $LaNi_{4.5}Al_{0.5}$ hydride phase: electronic properties and sites occupation*

Chen Dong(陈 东)[a)]†, Yu Ben-Hai(余本海)[a)], Wang Chun-Lei(王春雷)[a)], and Gao Tao(高 涛)[b)]

[a)] *Department of Physics, Xinyang Normal University, Xinyang* 464000, *China*

[b)] *Institute of Atomic and Molecular Physics, Sichuan University, Chengdu* 610065, *China*

(Received 1 November 2006; revised manuscript received 29 January 2007)

In this paper the crystal structure, electronic structure and hydrogen site occupation of $LaNi_{4.5}Al_{0.5}H_y$ hydride phase ($y = 5.0, 6.0$) have been investigated by using full-potential linearized augmented plane wave method. The hydrogen atoms were found to prefer the 6m, 12o and 12n sites, while no 4h sites were occupied. A narrowed Ni-d band is found due to the lattice expansion, the total density of states at E_F increases with y, which indicates that the compounds become less stable. The interaction between Al and Ni, H plays a dominant role in the stability of $LaNi_{4.5}Al_{0.5}H_y$ hydride phase. The smaller the shift of E_F towards the higher energy region, the more stable the compounds will be. The obtained results are compared with experimental data and discussed in the light of previous works.

Keywords: hydrogen storage materials, $LaNi_{4.5}Al_{0.5}$, hydride phase, electronic structure
PACC: 6155H, 7115A, 7120C

1. Introduction

The storage of hydrogen in the form of metal hydrides has been investigated for the last three decades.[1−4] $LaNi_5$ alloys are of great technological interest in their applications such as heat pumps, compressors, rechargeable batteries and energy conversion materials,[5,6] besides, $LaNi_5$–H system is accepted as a prototype of hydrogen absorbing materials for its excellent hydrogenation properties. However, partial substitution by M (M = Al, Co, Sn, Mn, Fe) for Ni in the $LaNi_5$ improves some practical properties of this hydrogen storage alloy.[7−9]

$LaNi_{5-x}Al_x$ ($0\leq x \leq 1.5$) alloys have been extensively investigated because of their interesting hydriding properties.[10,11] $LaNi_{4.5}Al_{0.5}$ is a very useful material because of its low plateau pressure and resistance to impurities in hydrogen gas. Al substitution for Ni in $LaNi_5$ alloy can drastically increase the cycle life time and the discharge capacity[12] without causing much decrease in hydrogen storage capacity[13] and decrease the activation energy.[14]

Comparing with the many investigations of the $LaNi_{4.5}Al_{0.5}H_y$ compounds, we find that little works have been carried out on the structure and the electronic properties of hydride phase (γ-phase) ($4.5 < y < 6$).[15] Sites occupation of H atoms and the electronic structures of the $LaNi_{4.5}Al_{0.5}H_y$ hydride phase are still unclear, in addition to the electronic structures. The Metal–H interactions have not been comprehensively understood.

In this paper, the electronic structures and the microarrangements of hydrogen atoms in $LaNi_{4.5}Al_{0.5}H_y$ hydride phase (γ-phase) have been studied by means of the full-potential linearized augmented plane wave (FLAPW) method. More information on the electronic structures of $LaNi_{4.5}Al_{0.5}H_y$ is obtained. The hydrogen occupied sites are also analysed, the calculated electronic properties have been compared with experimental results.

2. Crystal structures and computational methodology

$LaNi_5$ crystal has a hexagonal $CaCu_5$ structure (space group P6/mmm). The La atom occupies the 1a (0, 0, 0) Wyckoff site. The two nonequivalent Ni atoms occupy the 2c (2/3, 1/3, 0) and the 3g (0, 0.5, 0.5) Wyckoff sites. X-ray powder diffraction[16] shows that the $LaNi_{5-x}Al_x$ alloys still retain the $CaCu_5$ structure until $x \leq 1.3$. Al atoms prefer 3g sites in

---

*Project supported by the National Natural Science Foundation of China (Grant No 10276027).

†Corresponding author. E-mail: chchendong2010@163.com

$LaNi_4Al$[17,18] and this fact was verified by total energy calculations.[12] Based on these results, we build a double unit cell along c axis of $LaNi_5$ unit cell. Al atom substitutes Ni atom in the 3g (0.5a, 0.5b, 0.75c) site as shown in Fig.1.

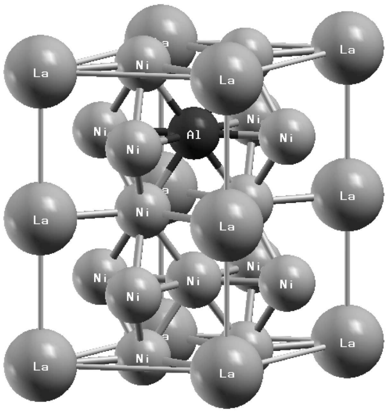

Fig.1. The double unit cell used for $LaNi_{4.5}Al_{0.5}$ ternary alloys.

In $LaNi_5$ alloys there are five nonequivalent interstices which have been reported to be available to store hydrogen atoms.[19] There are ten nonequivalent interstices in the double unit cell: 3f* (La_2Ni_4), 4h* (Ni_4), 6m* (La_2Ni_2), 12n* (La_1Ni_3), 12o* (La_1Ni_3), 3f ($La_2Ni_3Al_1$), 4h (Ni_3Al_1), 6m (La_2Ni_2), 12n ($La_1Ni_2Al_1$) and 12o (La_1Ni_3). The sites marked without '*' denote the sites in the Al-substituted unit cell, moreover, the sites marked with '*' represent the unchanged $LaNi_5$ unit cell. Based on the Westlake's two criterions, namely: (a) the minimum interstitial size is 0.4 Å; (b) the minimum H–H distance is 2.1 Å,[20] several models are built for $LaNi_{4.5}Al_{0.5}H_y$ ($y = 5.0, 6.0$). The hydrogen occupied sites, lattice constants, E_F and total energy are shown in Table 1 and Table 2. Because Percheron-Guégan *et al*[17], and Crowder and Jame,[21] maintained that the $LaNi_{5-x}Al_x$ hydrides and deuterated compounds still belong to the P6/mmm space group, the P6/mmm space group was retained in the following calculation.

The calculations have been performed by using the density functional theory (DFT) in the generalized gradient approximation (GGA). We have used the FLAPW method.

The GGA of Perdew, Burke and Ernzerhof[22] (PBE96) was used for the exchange–correlation energy functional. Atomic geometries were obtained by minimizing the Hellman–Feynman[23,24] forces, and the Pulay scheme is used for a more rapid convergence.

In our calculations the plane wave cutoff energy was chosen as 280eV in order to get a good plane wave basis set. K-point grids have 128 k-points in the irreducible Brillouin zone (IBZ) of $LaNi_{4.5}Al_{0.5}H_y$ ($y = 5.0, 6.0$). The force components on each atom were relaxed to 10^{-3}eV/A and the energy convergence were set to less than 0.0002eV. The density of states (DOS) is calculated with the linear energy tetrahedron method in a mesh of 0.0002 eV.

Table 1. Calculated values of the lattice constants, E_F and Energy for $LaNi_{4.5}Al_{0.5}H_{5.0}$

sites occupation	a/nm	c/nm	E_F	Energy/Ry
6m, 12o*, 3f, 6m*, 3f*, 6m*, 12n, 12o, 6m, 12n*	0.5194	0.4580	0.6771	−61862.7397
6m, 12o*, 3f, 6m*, 3f*, 6m*, 12n, 12o 3f*, 12o	0.5216	0.4568	0.6751	−61862.7376
6m, 12o*, 3f, 6m*, 3f*, 6m*, 12n, 12o, 12n*, 4h	0.5210	0.4549	0.6761	−61862.7371

Table 2. Calculated values of the lattice constants, E_F and Energy for $LaNi_{4.5}Al_{0.5}H_{6.0}$.

sites occupation	a/nm	c/nm	E_F	Energy/Ry
6m, 12o*, 3f, 6m*, 3f*, 6m*, 12n, 12o, 6m, 12n*, 6m, 12n	0.5221	0.4690	0.6649	−61864.8125
6m, 12o*, 3f, 6m*, 3f*, 6m*, 12n, 12o, 6m, 12n*, 4h*, 6m	0.5127	0.4596	0.6618	−61864.7568
6m, 12o*, 3f, 6m*, 3f*, 6m*, 12o*, 12n, 6m, 12n*, 12o, 12n	0.5160	0.4618	0.6610	−61864.7725

In Table 1, it is found that the hydrogen atoms prefer to occupy 6m and 6m* sites, in accord with Ref.[25]. From Table 2, it seems that as long as 6m* and 6m sites, hydrogen atoms also prefer the 12n and 12o sites. We conclude that the hydrogen atoms prefer the 6m, 12n and 12o sites, no 4h sites were occupied.

3. Results and discussion

3.1. Optimized structures

The calculated lattice constants for $LaNi_{4.5}Al_{0.5}H_y$, the total DOSs at E_F and the electronic specific heat coefficients are listed in Table 3.

Table 3. The lattice constants for $\mathrm{LaNi_{4.5}Al_{0.5}}$, total DOS at E_F and γ for $\mathrm{LaNi_{4.5}Al_{0.5}H}_y$ $(y = 5.0, 6.0)$.

	$\mathrm{LaNi_{4.5}Al_{0.5}H_{5.0}}$	$\mathrm{LaNi_{4.5}Al_{0.5}H_{6.0}}$		$\mathrm{LaNi_{4.5}Al_{0.5}}$
a	0.5194 nm	0.5221 nm	a(cal)	0.5057 nm
c	0.4580 nm	0.4690 nm	c(cal)	0.4093 nm
$n(E_\mathrm{F})$	14.77	15.58	a(exp)	0.5038 nm[26]
γ	34.83	36.75	c(exp)	0.4007 nm[26]

So far there is no experimental lattice constants available for $\mathrm{LaNi_{4.5}Al_{0.5}H}_y$ $(y = 5.0, 6.0)$, in this instance the lattice constants of $\mathrm{LaNi_{4.5}Al_{0.5}}$ are calculated and compared with experimental data. The calculated lattice constants are in excellent accord with the experimental values. The electronic specific heat $\gamma = (\pi^2/3)k_\mathrm{B}^2 n(E_F)$,[14] where k_B is Boltzmann's constant. We found that the lattice expansion is mainly along the c axis, the compound becomes less stable. The total DOS at E_F increases from 14.77 to 15.58 states/eV.f.u, the corresponding coefficients of the electronic specific heat are 34.83 and 36.75mJ/mol $\mathrm{LaNi_{4.5}Al_{0.5}H}_y$–$\mathrm{K}^2$.

3.2. Densities of states

The origin of the energy scale is located at the Fermi energy E_F. Total and partial DOSs of $\mathrm{LaNi_{4.5}Al_{0.5}H}_y$ $(y = 5.0, 6.0)$ are shown in Fig.2 to Fig.4. Because the partial DOSs of $\mathrm{LaNi_{4.5}Al_{0.5}H_{6.0}}$ are similar to the partial DOSs of $\mathrm{LaNi_{4.5}Al_{0.5}H_{5.0}}$, they are not shown.

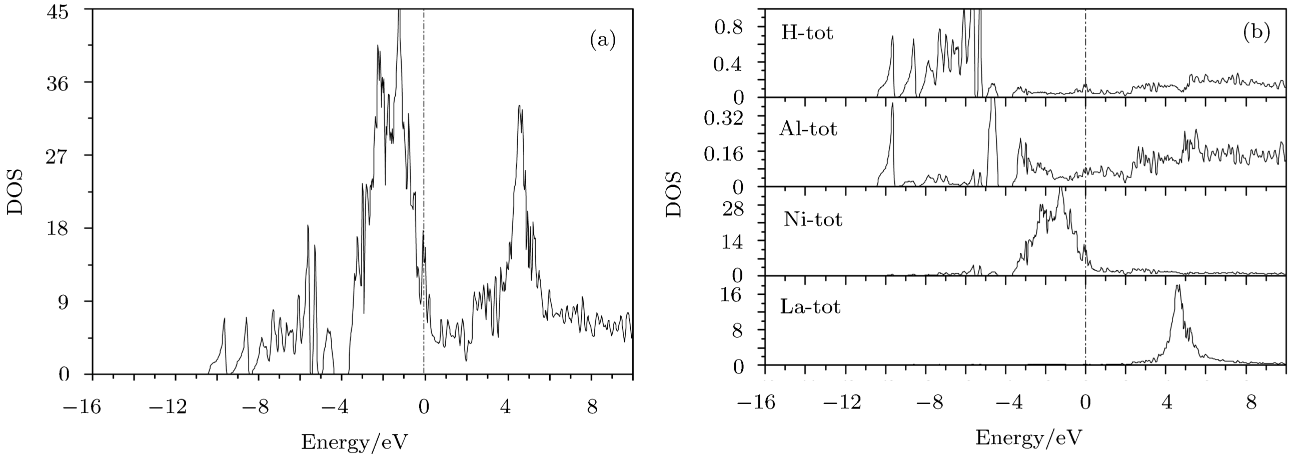

Fig.2. Spin-averaged total DOS for $\mathrm{LaNi_{4.5}Al_{0.5}H_{5.0}}$ (a) and partial DOSs projected onto H, Al, Ni, La (b).

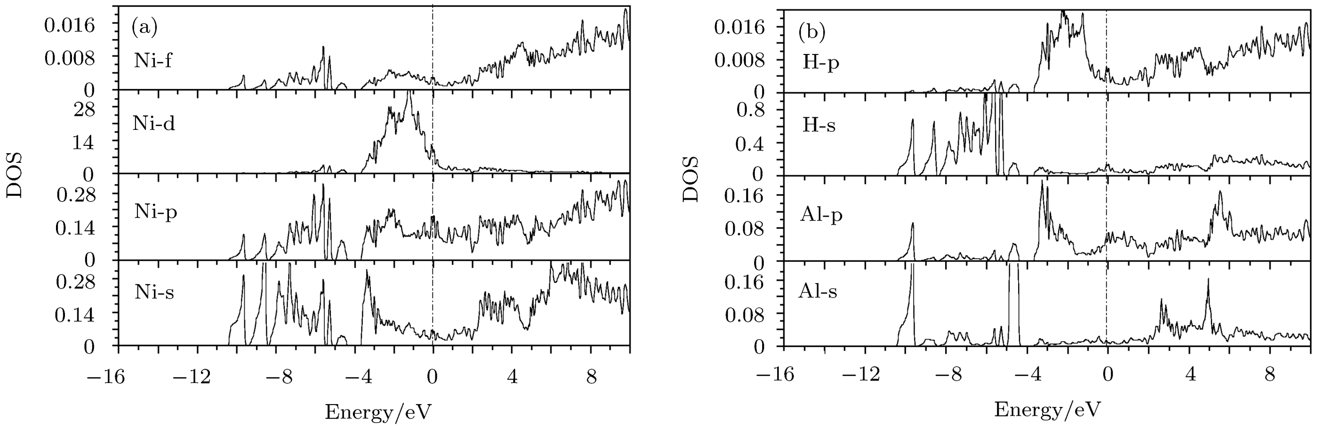

Fig.3. Spin-averaged partial DOSs projected onto Ni (a) and H, Al (b) in $\mathrm{LaNi_{4.5}Al_{0.5}H_{5.0}}$.

In Figs.2 and 4, the total DOSs of $LaNi_{4.5}Al_{0.5}H_y$ ($y = 5.0, 6.0$) are shown, with a double unit cell. The total DOSs at Fermi energy E_F are dominated by the contribution of the Ni-d bands. The increase of hydrogen atoms from 5.0 to 6.0 results in a broadening of the total DOSs and a narrowing of Ni-d bands.

The Fermi energy E_F goes up at the top of the Ni-d bands and shifts towards the high energy states with y. The Ni-d bands are not entirely filled, which indicates that the $LaNi_{4.5}Al_{0.5}H_y$ becomes less stable with the increase of y. Refs.[27,28] show that the Ni-d bands are entirely filled in $LaNi_4Al$ crystal, but in our calculation the Ni-d bands are not completely filled in $LaNi_{4.5}Al_{0.5}H_y$. We conclude that the addition of hydrogen atoms make the La–Ni–Al hydride unstable. The increase of total DOSs at E_F is mainly induced by the increase of Ni-d bands at E_F.

It is clear from Fig.4(a), E_F remains located at the upper extreme of the Ni-3d bands. Figure 4(b) displays partial DOSs for H, Al, Ni and La. Hydrogen-derived bands are mainly located at −10.5 eV to −4.5 eV below E_F. The value of DOSs located around −10.5 eV to −4.5 eV of Al and H increases, which indicates that Al–H interaction is enhanced. Bonding interactions between Al–Ni and Al–H can play a role in improving the cycling life time and stability of $LaNi_{4.5}Al_{0.5}H_y$ compounds. When y increases from 5.0 to 6.0, the Ni-d bands are narrowed due to a decrease in the Ni–Ni interaction. In the hydride phase, the contribution of Ni-d bands at E_F remains bigger than that of the La-d bands in comparison with Refs.[29,30].

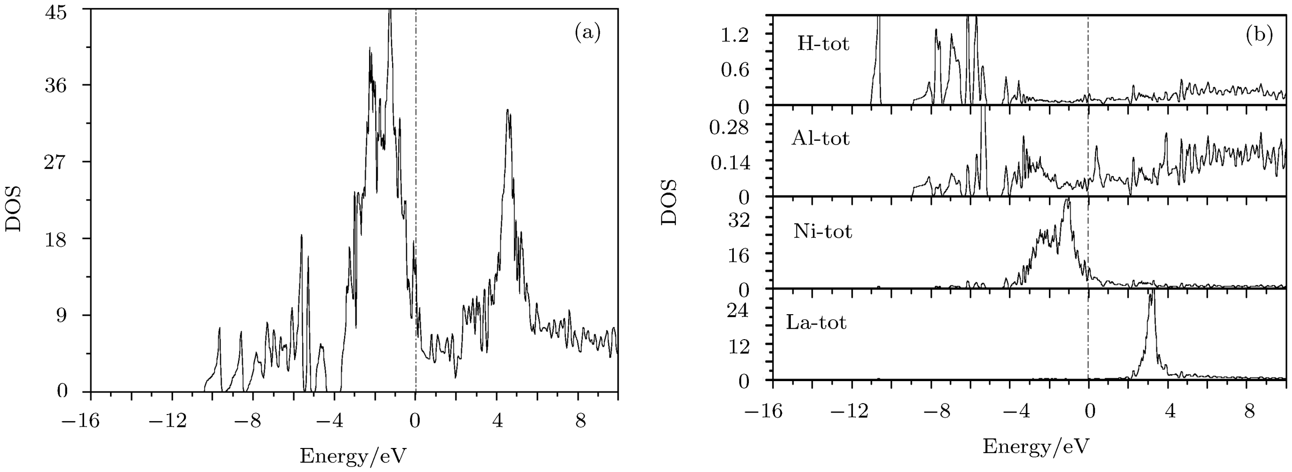

Fig.4. Spin-averaged total DOS for $LaNi_{4.5}Al_{0.5}H_{6.0}$ (a) and partial DOSs projected onto H, Al, Ni La (b).

In Fig.3(b), the Al-s and H-s bands are located at −10.5 eV to −4.5 eV, while the Al-p and H-p bands are located at higher energy region (−4.5 eV to −2 eV). The bonding interactions of the H-s with Al-s, and Ni bands are the dominators of the total DOSs at −10.5 eV to −4.5 eV, the H–La interaction is much smaller than the H–Ni interaction. The contribution of H-p and Ni-d interaction is small but non-negligible. It is clear that the chemical bonding interaction of H with Ni and Al plays a role in improving the stability of the $LaNi_{4.5}Al_{0.5}H_y$ compounds. Ni–H interaction is the dominator of the metal–hydrogen bonding interaction bands. Al–H interaction is the second important component in the metal–hydrogen bonding.

We find three factors that affect the stability of the $LaNi_{4.5}Al_{0.5}H_y$ compounds:

(I) The contribution of Al–H and Al–Ni bonding at low energy region. The compound will be more stable if the contribution is higher.

(II) The location of E_F. If E_F locates at the bottom of the valley, the compound will be stable.

(III) The shift of E_F towards higher energy region. If it is smaller than the corresponding $LaNi_5H_y$ compounds, it is more stable than $LaNi_5H_y$.

3.3. Charge distributions

The charge distributions for $LaNi_{4.5}Al_{0.5}H_y$ ($y = 5.0, 6.0$) are shown in Figs.5 and 6. Bond charges between the hydrogen atoms and the metal atoms are shown. It is clear that the highest charge density resides in the immediate vicinity of the atomic nuclei. As we expected, the hydrogen atoms locate in the low-density regions of the alloy, namely, the interstice regions. No localized bond charge can be seen, it suggests that the M–H (M = La, Ni, Al) interactions are ionic.

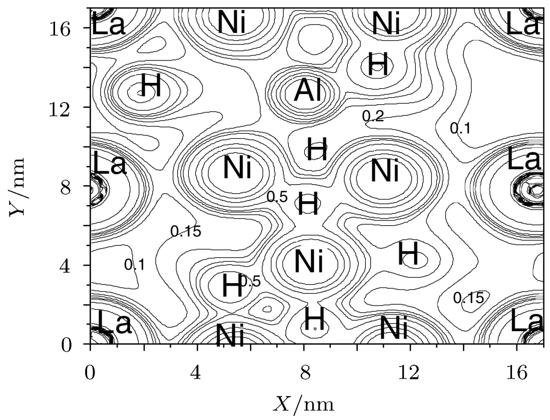

Fig.5. Charge density of $\mathrm{LaNi_{4.5}Al_{0.5}H_{5.0}}$ for the $(11\bar{2}0)$ plane (Innermost contour 10.0 a.u.$^{-3}$, outer-most 0.1 a.u.$^{-3}$).

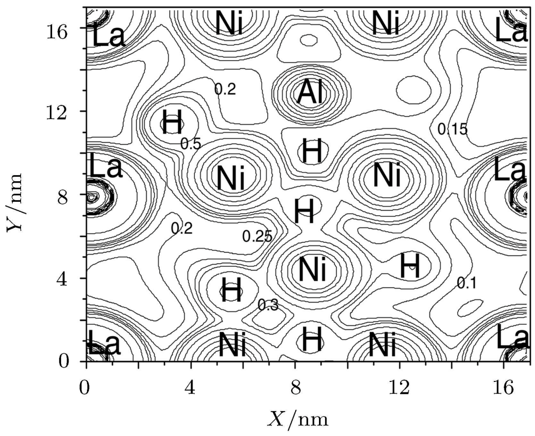

Fig.6. Charge density of $\mathrm{LaNi_{4.5}Al_{0.5}H_{6.0}}$ for the $(11\bar{2}0)$ plane. (Innermost contour 10.0 a.u.$^{-3}$, outer-most 0.1 a.u.$^{-3}$)

In Fig.5 no clear La–H bonding can be seen. The electron cloud of hydrogen atom disperses mainly through the Ni–H direction. In Fig.6 it is clear that the Al–H bonding ($\sim$ 0.25 a.u.$^{-3}$) is weaker than the Ni–H bonding ($\sim$ 0.5 a.u.$^{-3}$), but stronger than the La–H bonding.

Finally, we can see the decreasing strength of metal–Hydrogen bonding while going from Ni–H (strongest), to Al–H (intermediate) to La–H (weakest) in Figs.5 and 6.

4. Conclusions

By building a double unit cell, we have analysed the microarrangements of hydrogen atoms, the crystal structures, stability and the electronic structures of $\mathrm{LaNi_{4.5}Al_{0.5}H}_y$ $(y = 5.0, 6.0)$ through all-electron calculations. Based on the calculations, we found that the hydrogen atoms prefer to occupy the 6m, 12o and 12n sites, no 4h sites were occupied, in accordance with Ref.[14]. We also give the most probable sites for hydrogen atoms in $\mathrm{LaNi_{4.5}Al_{0.5}H}_y$, they are listed in Table 1 and Table 2.

In the hydride phase of $\mathrm{LaNi_{4.5}Al_{0.5}H}_y$, the s bands of Al, H elements lead to an increase in the DOS located around -10.5 eV to -4.5 eV. The DOS at E_F remains high due to an important contribution of Ni-d bands. The addition of hydrogen atoms induces the increase of total DOSs at E_F, the calculated total DOS at E_F increases from 14.77 to 15.58 states/eV-f.u, the corresponding electronic specific heats are 34.83 and 36.75 mJ/mol $\mathrm{LaNi_{4.5}Al_{0.5}H}_y$–$\mathrm{K}^2$ respectively.

The DOS at E_F remains high due to an important contribution of Ni-d bands compared with $\mathrm{LaNi_5}$. A narrowed Ni-d band was found due to the lattice expansion. We also found that the greater stability of the $\mathrm{LaNi_{4.5}Al_{0.5}H}_y$ compared to $\mathrm{LaNi_5H}_y$ is mainly due to Ni–H, Al–Ni bonding and to a smaller shift of E_F towards higher energies.

References

[1] Mueller W M, Blackledge J P and Libowitz G G 1968 In *Metal Hydrides* (New York: Academic) p490

[2] Wipf H 1997 *Hydrogen in Metals III Topics in Applied Physics* (Heidelberg: Springer) **73** p51

[3] Anani A, Visintin A, Petrov K, Srinivasan S, Reilly J J, Johnson J R, Schwarz R B and Desch P B 1994 *J. Power Sources* **47** 261

[4] Zhu K G, Shi J Z and Zhang L D 1998 *Chin. Phys.* **7** 504

[5] Wiswall R in: 1978 Alefeld G and Volkl J (Eds), *Hydrogen in Metals II, Topies in Applied Physics* (Berlin: Springer) **29** p201

[6] Lin S J and Zheng H P 2005 *Acta Phys. Sin.* **10** 4680 (in Chinese)

[7] Sluiter M, Takahashi M and Kawazoe Y 1997 *J. Alloys. Compd.* **248** 90

[8] Gupta M 1999 *J. Alloys. Compd.* **293-295** 190

[9] Haraki T, Inomata N and Uchida H 1999 *J. Alloys. Compd.* **293-295** 407

[10] Mendelsohn M H, Gruen D M and Dwigh A E 1977 *Nature* **269** 45

[11] Mendelsohn M H, Gruen D M and Dwight A E 1979 *Adv. Chem. Series* **173** 279

[12] Szajek A, Jurczyk M and Rajewski W 2000 *J. Alloys. Compd.* **307** 290

[13] Nakamura Y, Nakamura H, Fujitani S and Yonezu I 1994 *J. Alloys. Compd.* **210** 299

[14] Oh J W, Kim C Y, Nahm K S and Sim K S 1998 *J. Alloys. Compd.* **278** 270

[15] Hubbard W N, Rawlins P L and Connick P A 1983 *J. Chem. Thermodymamics* **15** 785

[16] Jensen J O and Bjerrum N J 1999 *J. Alloys. Compd.* **293-295** 185

[17] Percheron-Guégan A, Lartigue C and Achard J C 1980 *J. Less-Common. Met.* **74** 1

[18] Lartigue C, Percheron-Guégan A, Achard J C and Tasset F 1980 *J. Less-Common. Met.* **75** 23

[19] Soubeyroux J L, Percheron-Guégan A and Achard J C 1987 *J. Less-Common. Met.* **129** 181

[20] Westlake D G 1983 *J. Less-Common. Met.* **91** 275

[21] Crowder C and James W J 1982 *J. Appl. Phys.* **53** 2637

[22] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865

[23] Feynman R P 1939 *Phys. Rev.* **56** 340

[24] Hellman H 1937 *Einfuhrung in Die Quantumchemie* (Leipzig: Deuticke) p1

[25] Du H L, Zhang W Y, Wang C S, Han J Z, Yang Y C, Chen B, Xie C M, Sun K and Zhang B S 2003 *Solid State Commun.* **128** 157

[26] Cao D L, Zhang R J, Leng H Y, Chen D M, Lu M Q and Yang K 2004 *Chinese Rare Earths* **25** 6 (in Chinese)

[27] Gupta M 2000 *Int. J. Quant. Chem.* **77** 982

[28] Paul-Boncour V, Gupta M, Joubert J M, Percheron-Guégan A, Parent P and Laffon C 2000 *J. Mater. Chem.* **10** 2741

[29] Gao T, Qi X H and Chen B 2005 *The Chinese Journal of Nonferrous Metals* **15** 1092 (in Chinese)

[30] Zhang R J, Wang Y M, Lu M Q, Xu D S and Yang K 2005 *Acta Materialia* **53** 3445