Electronic properties of LaNiIn doped with hydrogen[*]

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Electronic properties of RNiInH (R = La,Ce,Nd) intermetallic hydrides were recently studied both experimentally and theoretically. In the present work, we study the influence of hydrogen on the electronic structure of LaNiIn. The electronic structure is calculated by Augmented Spin Wave (ASW) and Tight Binding Linear Muffin Tin Orbital methods within the spin density approximation. The doped hydrogen atoms modify the band structure near the Fermi level. The density of states at the Fermi level decreases with increasing hydrogen concentration but the compounds have metallic character.

Key words: *hydrides; electronic structure; LaNiIn hydride; LMTO; ASW*

1. Introduction

Metal hybrids alloys are the most promising materials for hydrogen storage because of their hydrogen storage capacity. In the group of RTX intermetallics (R – rare earth metal, T – transition metal and X – p electron element), LaNiIn alloy doped with hydrogen has been studied experimentally and theoretically [1–7].

LaNiIn crystallizes in the ZrNiAl-type structure (space group No. 189) [7]. La atoms are located at 3g position: x, 0, 0.5; 0, x, 0.5; $-x$, x, 0.5 for $x = 0.593$ and $x = 0.6035$. In atoms occupy 3f positions: x, 0, 0; 0, x, 0; $-x$, $-x$, 0 for $x = 0.242$ and $x = 0.2437$. Ni is located at two positions; 1b: 0, 0, 0.5 and 2c: 1/3, 2/3, 0 and 0, 2/3, 1/3. Hydrogen can be distributed in 4h position (depending on the concentration) 1/3, 2/3, z; 1/3, 2/3, $-z$; 2/3, 1/3, z; 2/3, 1/3, $-z$ for $z = 0.659$.

Recently, Jezierski at al. [6] studied electronic structure of LaNiIn and LaNiInH$_x$ ($x = 1/3$, 2/3, 1) using the XPS and *ab initio* LMTO [9] methods. The theoretical re-

sults were compared with X-ray photoemission spectra (XPS). In this work, we report the influence of hydrogen on the electronic structure of LaNiInH$_x$ compounds by using the ASW [8] and LMTO [9] methods.

2. Method of calculation

Electronic properties of LaNiInH$_x$ compounds were calculated by *ab initio* augmented spherical wave (ASW) [8] and tight-binding linear muffin-tin orbital (TB LMTO) [9] methods within the framework of the local spin density approximation (LSDA). The exchange correlation potential was assumed in the form proposed by Barth and Hedin [10]. The scalar-relativistic approximation for band electrons and the fully-relativistic approximation of the frozen core electrons were used in both methods. The self-consistent calculations were performed in the atomic spheres approximation (ASA) for 459 (LMTO) and 469 (ASW) *k*-points in the irreducible Brillouin zone. The *ab initio* calculations of the band structure were performed for the experimental values of the lattice parameters [5]. For the ordered LaNiIn compounds we assumed $a = 7.5906$ Å and $c = 4.05$ Å. For the doped hydrogen compound, the calculations were made for $a = 7.381$ Å and $c = 4.6489$ Å [5]. The hydrogen atoms can occupy four positions (see Introduction) in ZrNiAl type structure. The electronic structures were calculated for one, two, three and four hydrogen atoms located in 4h position. For the given configuration we obtained the total and partial densities of states. Particularly, we pay attention to the change of the density of states at the Fermi level as well as the contribution of d bands to the density of states near the Fermi level.

3. Results and discussion

The total densities of states calculated by LMTO (solid line) and ASW (broken line) methods for LaNiIn and LaNiInH$_4$ alloys are presented in Fig. 1.
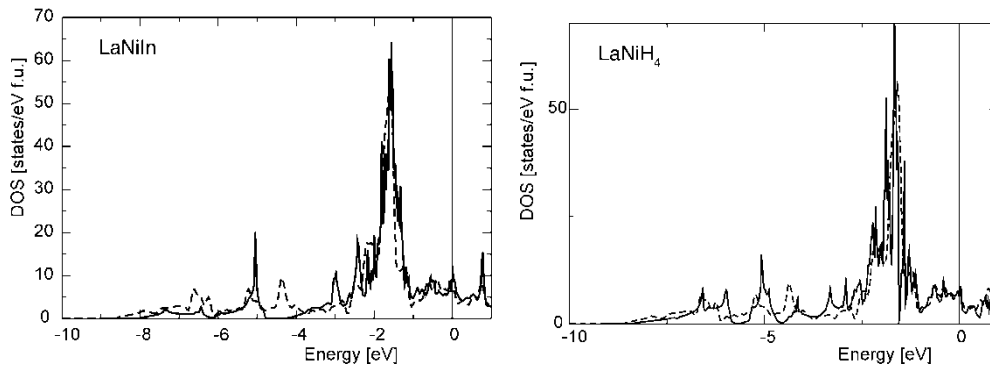

Fig. 1. Total density of states (TDOS) for LaNiIn and LaNiInH$_4$ obtained by LMTO (solid line) and ASW (broken line) methods. The Fermi energy is located at $E = 0$ eV

We observed only a small modification of the shape of the density of states. The density of states at the Fermi level for LaNiIn is 8.14 and 10.48 states/eV f.u. for LMTO and ASW, respectively. In the case of LaNiH4 $N(E_F) = 6.85$ and 6.76 states/eV f.u. for LMTO and ASW methods, respectively.
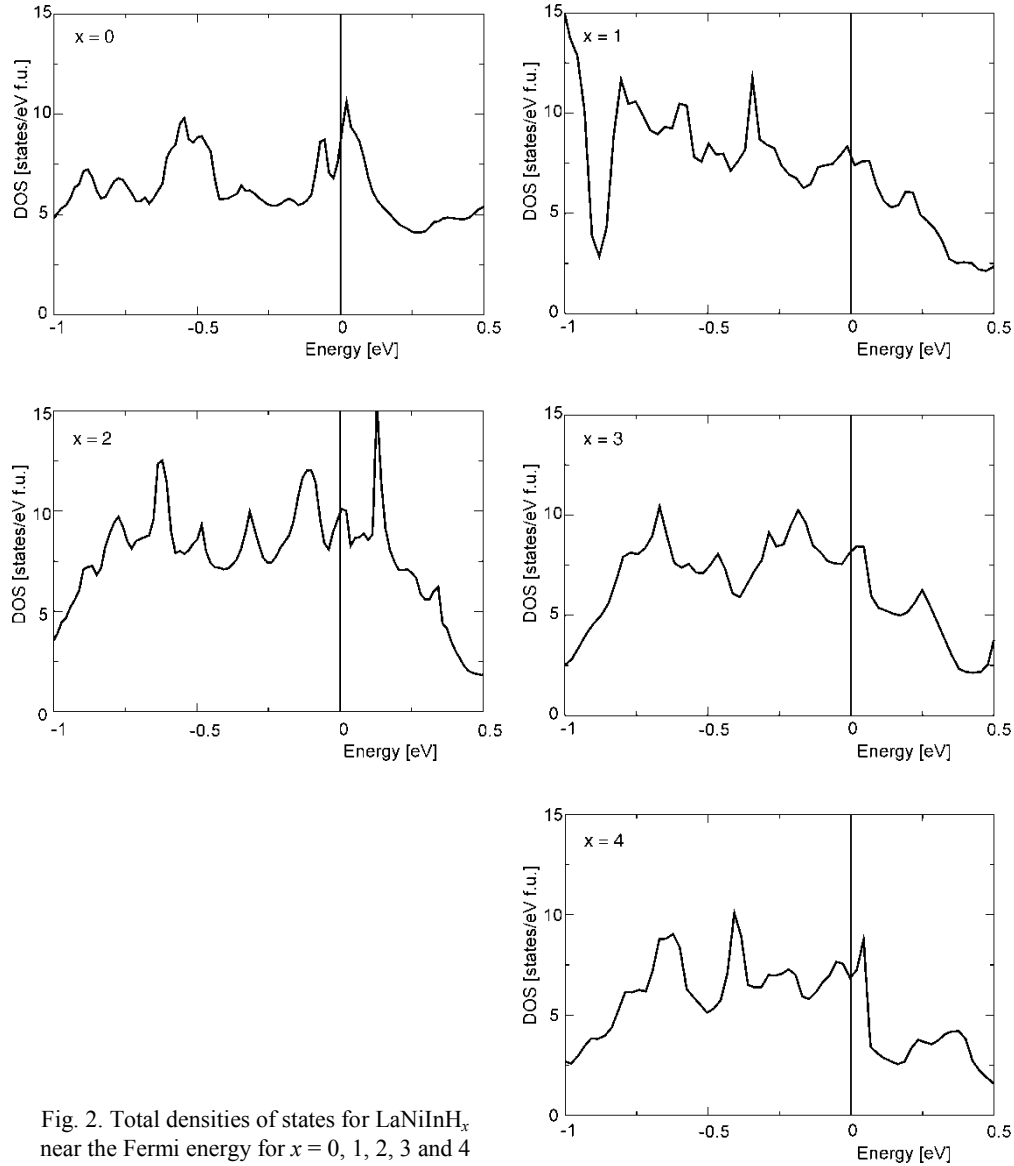

Fig. 2. Total densities of states for LaNiInH$_x$ near the Fermi energy for $x = 0, 1, 2, 3$ and 4

In Figure 2, we plotted total densities of states near the Fermi level for $x = 0, 1, 2, 3$ and 4 obtained by the LMTO method. We observe a strong modification of DOS for $-1.0 < E < 0.5$ eV. This change of the density of states is connected to hydrogen atoms

which change the local environment and symmetry of Ni and La atoms. The main contribution to the densities of states near the Fermi energy come from d states of La, Ni and In atoms. The local contributions from La(4d), Ni(3d) and In(3d) to the DOS near the Fermi level are plotted in Fig. 3 for various numbers of hydrogen atoms in the cell.
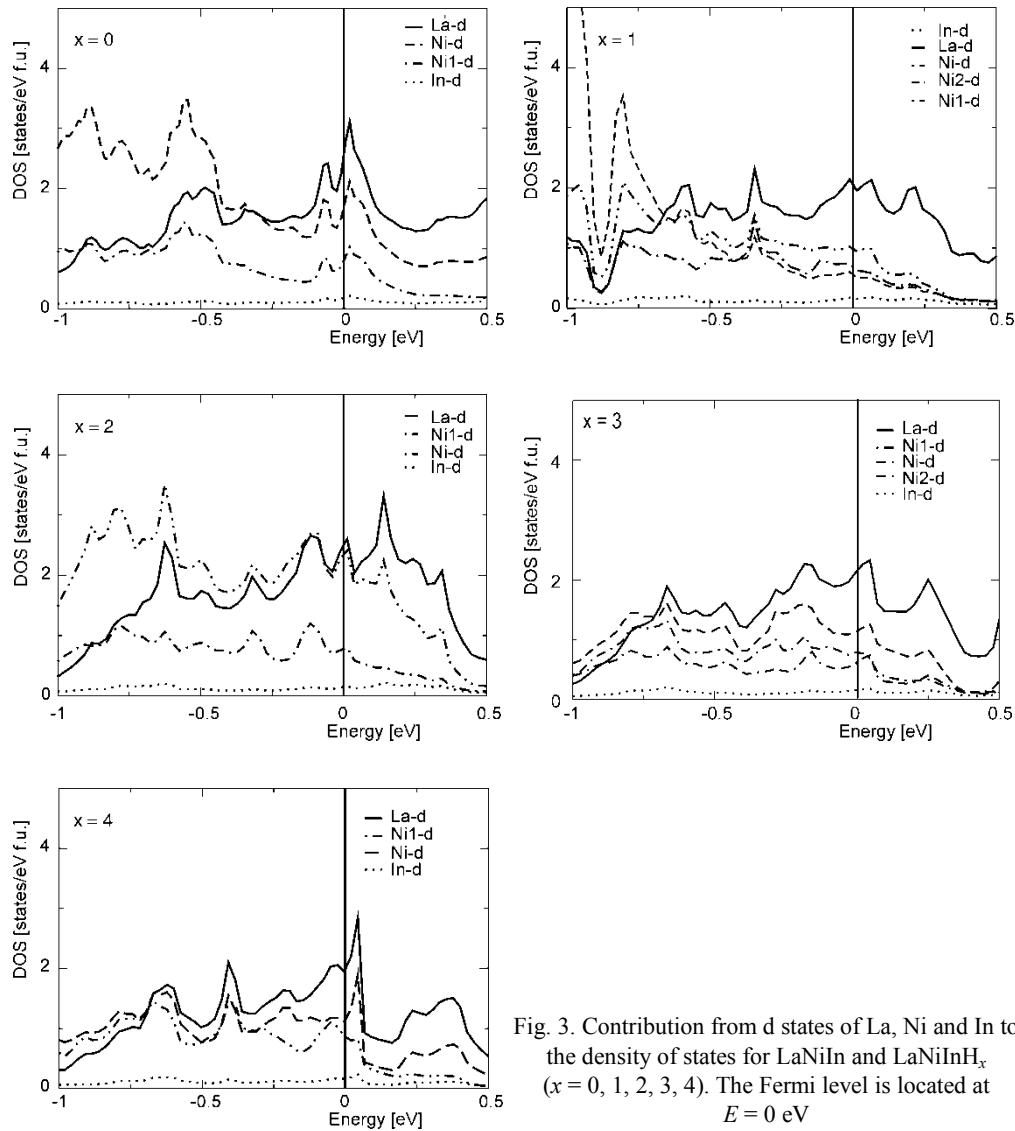

Fig. 3. Contribution from d states of La, Ni and In to the density of states for LaNiIn and LaNiInH$_x$ (x = 0, 1, 2, 3, 4). The Fermi level is located at $E = 0$ eV

Hydrogen atoms modify the shape of d states of La and Ni atoms. The substitution of hydrogen in LaNiIn leads to a change of the local symmetry around Ni. This effect gives two or three types of nickel atoms in the unit cell. The ASW and LMTO calculations for pure LaNiIn had shown that the valence band had well localized Ni 3d elec-

trons band near –1.6 eV. The peak located between –5 to –7 eV is due to In 4d electrons. The La 5d bands are located in the energy range from $E = -3$ to 1 eV. The band calculations suggest metallic character of LaNiIn alloys doped with hydrogen.
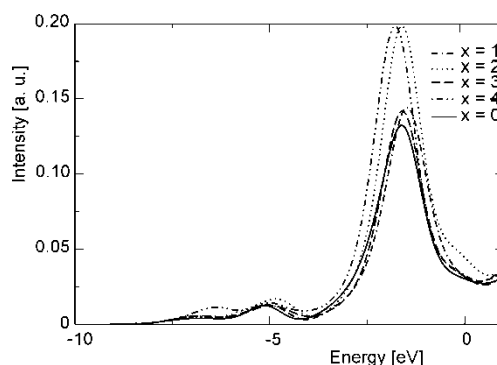
Fig. 4. Theoretical photoemission spectra for LaNiInH$_x$ ($x = 0, 1, 2, 3, 4$). The Fermi energy is located at $E = 0$ eV

In Figure 4, we present the calculated theoretical photoemission spectra of LaNiInH$_x$ ($x = 0, 1, 2, 3, 4$) obtained from the calculated partial density of states convoluted by Gaussian line with a half-width equal to 0.4 eV and scaled using proper photoelectric cross section for partial states [11] for various numbers of hydrogen atoms. We observe a small modification of the main peak with the change of the hydrogen concentration. The peak located near $E = 1.6$ eV was also observed in the XPS measurement [6].

4. Conclusions

The influence of doped hydrogen on the electronic density of states of LaNiInH$_x$ has been investigated. The shapes of the total densities of states obtained by LMTO and ASW methods are similar. In both methods, we observed a modification of the electronic density of states during the increase of the concentration of the hydrogen. The density of states at the Fermi level decreases when the number of hydrogen atoms increases.

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