

Electronic structures of LaNiIn and LaNiInH_x ($x = \frac{1}{3}, \frac{2}{3}, 1$ and $\frac{4}{3}$)

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Abstract

First-principle studies of the electronic structure of LaNiInH_x for $x = 0, \frac{1}{3}, \frac{2}{3}, 1$ and $\frac{4}{3}$ are performed using the spin-polarized tight binding linear muffin-tin orbital (TBLMTO) method. These compounds crystallize in the ZrNiAl-type crystal structure. For LaNiIn, a gap occurs (between -5.0 and 4.2 eV), below which the s-states of In and Ni atoms are present. In the energy range from -4.2 eV to E_F , there is a large number of electronic states with mainly La 5d, Ni 3d and In 5p character. The doped hydrogen atoms change the electronic structure. Low concentration of hydrogen ($x \leq \frac{2}{3}$) gives the additional H 1s band in the lower part of the valence band in the -4.0 and -6.0 eV region which destroys the energy gap. With increasing hydrogen content for $x = 1, \frac{4}{3}$ the H 1s band broadens (-1.5 to -8 eV). The calculations of the density of states at the Fermi level show that the studied materials have metallic character.

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1. Introduction

The most attractive aspect of metal hydrides from a technological point of view is their potential use as energy storing materials. RTX intermetallics (R = rare earth metal, T = transition metal and X = *p*-electron element) are between compounds for which influence of the hydrogenation on the electronic and magnetic properties is intensively studied. RNiIn compounds crystallize in the ZrNiAl-type structure (space group $P\bar{6}2m$) [1] and can formally be considered as a layered arrangement with a repeated stacking of two different planar nets of composition R_3Ni_2 and $NiIn_3$ along the [001] direction of the hexagonal unit cell. LaNiIn, CeNiIn and NdNiIn activate by hydrogen form the stable LaNiInH_{2.0}, CeNiInH_{1.8} and NdNiInH_{1.7} compounds [2]. Crystal structure of deuterides RNiInD_x (R = La, Ce and Nd) determined on the basis of high-resolution powder X-ray and neutron diffraction data is also the ZrNiAl-type [3]. These results indicate that hydrogenation or deuteration

does not influence the crystal structure of these compounds. In contrast the hydrogenation influences some physical properties. For example hydrogenation of CeNiIn induces the cerium valence transition from the intermediate to the trivalent state and induces ferromagnetic properties [4]. Proton magnetic resistance studies suggest that H atoms occupy the 4h and 6i sites [5,6] while X-ray and neutron diffraction studies [3] of RNiInD_{1.333-x} (R = La, Ce, Nd) compounds show that deuterium occupies the 4h site, located on the three-fold axis of the R₃Ni tetrahedra. The calculations of the electronic structure of ideal and fully saturated hydrides with composition RNiInH_{1.333} (R = La, Ce, Pr, Nd) compounds, based on the full-potential linear muffin-tin orbital, give the results which indicate a bonding between Ni and H atoms and a weak metallic bonding between H–H [7–9]. This work reports calculations of the electronic structure of the LaNiInH_x compounds for $x = 0, \frac{1}{3}, \frac{2}{3}, 1, \frac{4}{3}$. Because the calculated partial density of states is a useful tool to analyse the nature of chemical bonding in solids, from this data the influence of the doped hydrogen on the electronic structure is determined. The data for pure LaNiIn were compared with the X-ray photoemission spectroscopy (XPS) measurements.

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2. Experimental details and results

The X-ray photoemission spectra (XPS) were obtained at room temperature using the Leybold LHS10 electron photoemission spectrometer with Mg K α ($h\nu = 1253.6$ eV). The binding energies are referred to the Fermi level ($E_F = 0$). The electronic structure was studied by self-consistent tight-binding linearized muffin-tin orbital (TBLMTO) method [10]. The band calculations were performed within local spin density approximation (LSDA) for the exchange correlation potential in the form proposed by von Barth and Hedin [11] and Langreth and Hu [12]. The TBLMTO calculations were performed for 460–816 K points in the irreducible Brillouine zone. For the LaNiInH $_x$ systems, the band structure calculations were based on the crystal structure determined in Ref. [3] in which the atoms occupy the following positions:

- La atoms in 3g site: $x_1, 0, \frac{1}{2}; 0, x_1, \frac{1}{2}; \bar{x}_1, \bar{x}_1, \frac{1}{2}; x_1 \approx 0.595$
- Ni atoms in 1b site: $0, 0, \frac{1}{2}$ and 2c site: $\frac{1}{3}, \frac{2}{3}, 0; \frac{2}{3}, \frac{1}{3}, 0$
- In atoms in 3f site: $x_2, 0, 0; 0, x_2, 0; \bar{x}_2, \bar{x}_2, 0; x_2 \approx 0.25$
- H atoms in 4h site: $\frac{1}{3}, \frac{2}{3}, z; \frac{1}{3}, \frac{2}{3}, \bar{z}; \frac{2}{3}, \frac{1}{3}, z; \frac{2}{3}, \frac{1}{3}, \bar{z}; z$ changes from 0.587 for $x = 0.48$ to 0.676 for $x = 1.22$ [3].

The values of the lattice parameters and the positional parameters x_1 , x_2 and z reported in Ref. [3] were used. The calculated band structures of LaNiInH $_x$ for $x = 0, \frac{1}{3}, \frac{2}{3}, 1$ and $\frac{4}{3}$ are shown in Fig. 1. The data for $x = 0$ and $\frac{4}{3}$ are similar to those reported in Ref. [7]. For LaNiIn three low-lying bands originate from In 5s and Ni 4s electrons. Hybridized In 5p, Ni 3d and La 5d bands are present in the energy range from -3 to -1 eV. Near -4.5 eV, the energy gap is observed. The introduced hydrogen atoms give the additional s-band. For $x \leq \frac{2}{3}$, this band is in the region of In 5s and Ni 4s bands and does not destroy the energy gap but larger H concentration leads to disappearance of the energy gap.

The calculated partial and total density of states (DOS) for LaNiInH $_x$ for $x = 0, \frac{1}{3}, \frac{2}{3}, 1$ and $\frac{4}{3}$ are shown in Fig. 2. The results obtained for pure LaNiIn indicate that the valence band is predominate by well-localized band at -1.6 eV, which originates from the Ni 3d electrons. In the energy range -4.2 eV to the Fermi level, a large number of electronic states of mainly La 5d, La 6s, Ni 4s and In 5p character is present. The states are energetically degenerated, which implies that it is possible to form covalent Ni(1b)–La, Ni(2c)–La, La–In, Ni(1b)–In and Ni(2c)–In bonds. The interatomic Ni(1b)–3In and Ni(2c)–In distances are much shorter than Ni(2c)–La [3].

Hence the formation of covalent bonding between Ni(1b) or Ni(2c) and In is favorable both from energetically and spatial point of view. Between -4.2 and -5.0 eV, the gap occurs, below which the In 5s states form a narrow band. The unoccupied La 4f states are found in the conduction band region about 2.5 eV above E_F . These results are compared with the experimental data. Fig. 3 shows the XPS valence band of LaNiIn. Near the Fermi level (about 1 eV), the peak corresponding to the Ni 3d band is observed. Two additional

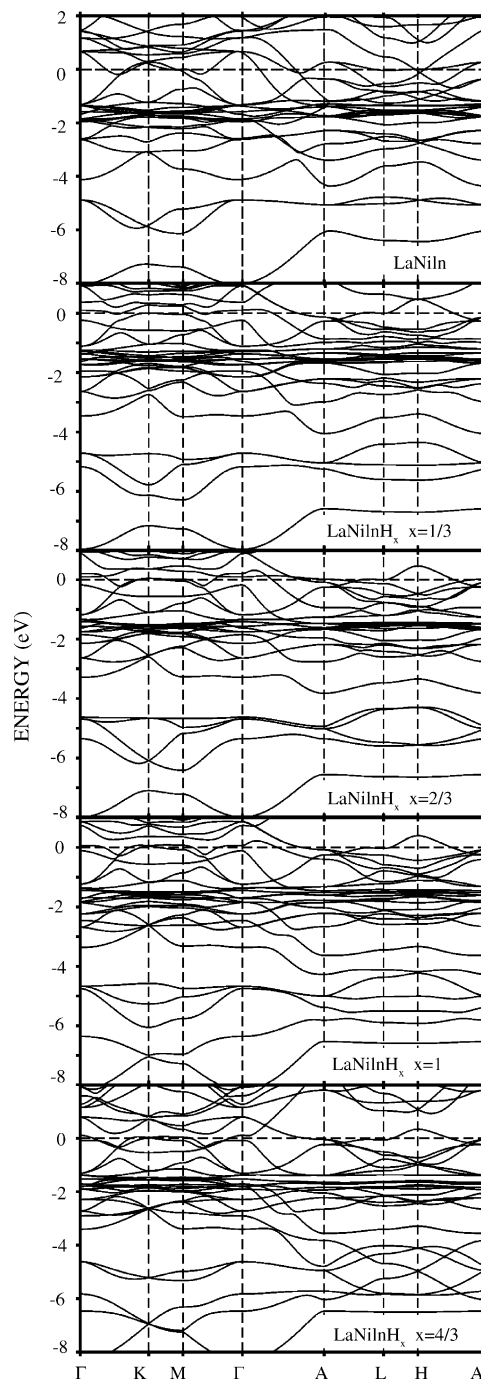


Fig. 1. Energy bands $[E(k)]$ for LaNiInH $_x$ ($x = 0, \frac{1}{3}, \frac{2}{3}, 1$ and $\frac{4}{3}$). High-symmetry directions in the Brillouin zone are marked. The Fermi energy is set to zero.

peaks at 6 and 8 eV correspond to the In 5s state and impurity oxygen on the surface.

In general, hydrogen atoms introduced into the LaNiIn matrix modify the electronic structure of most compounds by the creation of metal–hydrogen bonding states. The density of states of the compounds with $x \leq \frac{2}{3}$ give the additional H 1s band in the lower part of the valence band in the energy region between -4.0 and -6.0 eV. The increase of the hydro-

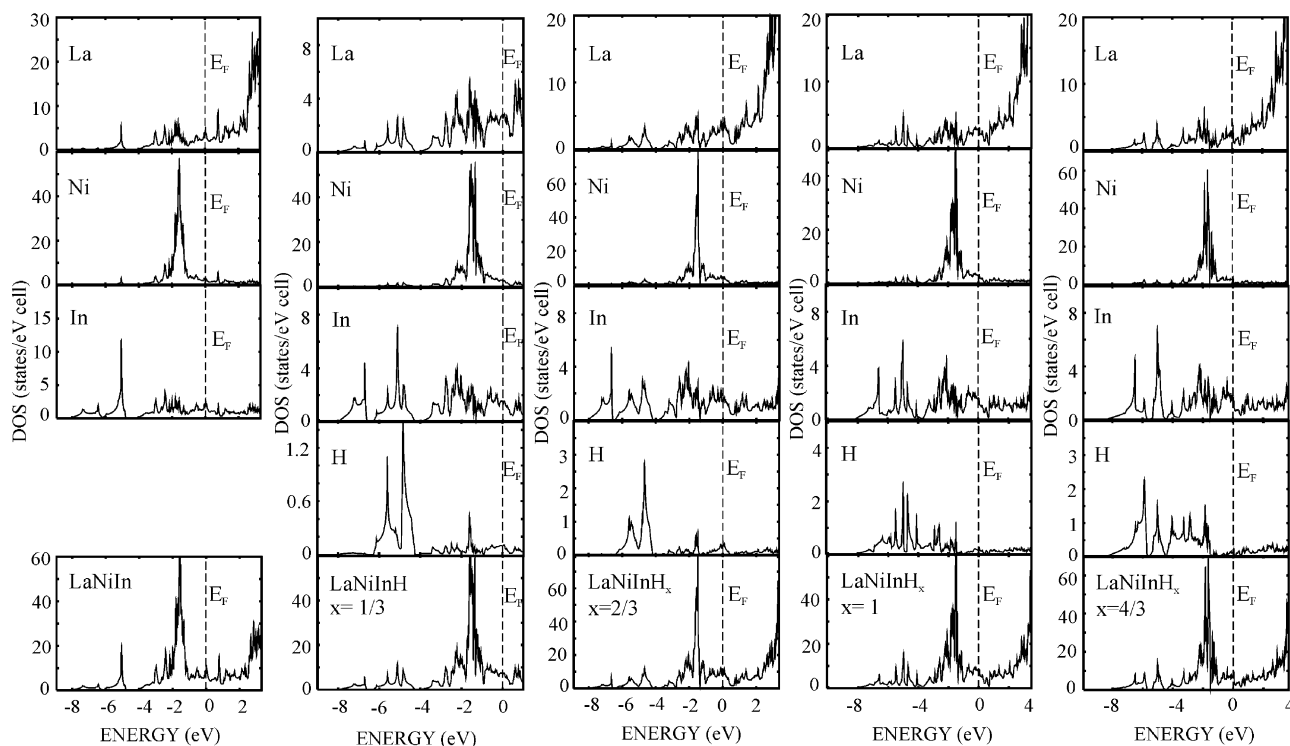


Fig. 2. Partial and total density of states for LaNiInH_x ($x = 0, \frac{1}{3}, \frac{2}{3}, 1$ and $\frac{4}{3}$). The Fermi level is located at $E_F = 0$ eV.

gen content ($x = 1, \frac{4}{3}$) causes the broadening of the H 1s band between -1.5 and -8 eV. These implying a possible covalent bonding contribution for the Ni–H, La–H, In–H and H–H atoms. Another interesting consequence for the DOS upon hydrogenation is that the In 5s states broaden as a results of the reduced interatomic distance between Ni and In. With

increasing hydrogen content the width of the energy gap decreases also down to zero for $x = 1$. The obtained results indicate that the doped hydrogen atoms practically do not influence the Ni 3d, La 5d and La 6s bands. The total density of states near the Fermi level form a broaden peak. The calculated density of states at the Fermi level changes from 8.42 states/eV f.u. for $x = 0$ by 6.83 states/eV f.u. for $x = \frac{1}{3}$, 9.87 states/eV f.u. for $x = \frac{2}{3}$, 7.98 states/eV f.u. for $x = 1$ and 6.75 states/eV f.u. for $x = \frac{4}{3}$. This results, which suggest a slight change of the density of state at E_F are in good agreement with the results of the NMR studies [13]. These result suggests metallic character of all these compounds. Similar conclusions on the metallic character of the isostructural $\text{RNiInH}_{1.333}$ ($R = \text{La, Ce, Nd}$) are reported in Ref. [7].

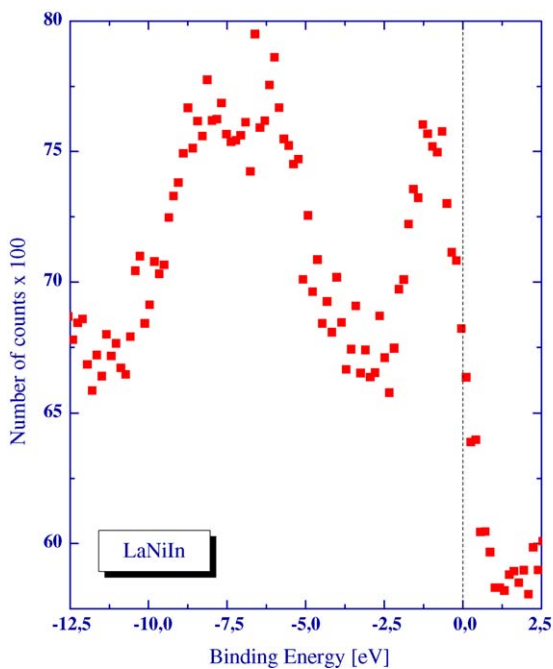


Fig. 3. XPS spectra of the valence band of LaNiIn .

3. Conclusion

We have investigated the influence of the doped hydrogen on the electronic structure of the LaNiInH_x ($x = 0, \frac{1}{3}, \frac{2}{3}, 1, \frac{4}{3}$) compounds with the ZrNiAl-type crystal structure using self consistent TBLMTO method. Our studies allow to draw the conclusion that the H atoms introduced into the RNiIn matrix change the electronic structure of the compound. The obtained data were analyzed with regard to the change of the crystal structure with increasing of H content. According to the X-ray and neutron diffraction data [3] in the $\text{LaNiInH}_{1.33}$ compound, hydrogen atoms are located inside the La_3Ni tetrahedral that share a common face to form trigo-

nal bipyramid. This configuration gives rise to extraordinary short H–H separation of about 1.6 Å [3]. The neutron diffraction data for isostructural LaNiInD_x for $x = 0.48$ and 1.22 give the following change of the interatomic distances with increasing deuterium content: La–D increases from 2.362(4) to 2.407(2) Å, Ni–D decreases from 1.68(1) to 1.507(4) Å. In LaNiInD_{0.48} the partly filled D sites are situated just 0.71(3) Å apart [3]. Since the site occupancy is less than one half, two neighbouring sites are most probably never simultaneously occupied. In practice this implies that the D–D separations is larger than 3 Å along the *c*-axis and larger than 4 Å in the basal plane. In LaNiInD_{1.2}, the D atoms form the pairs with the D–D distance equal 1.635 Å. Pairing of the hydrogen atoms has been applied to explain the anomalous proton magnetic resonance spectrum of CeNiInH_{1.0} [5]. This drastic change in the interatomic distances was found to reflect in the electronic structure. For the compounds with $x \leq \frac{2}{3}$ (the 4h site is half occupied), the H 1s level forms a sharp band between –4 and –6 eV. With increasing hydrogen content ($x > \frac{2}{3}$), the H 1s band broadens (between –1.5 and –8.0 eV) (see Fig. 2). The our density of state and presented in Ref. [7] as well as valence charge density, charge transfer plot, and electron localization function analysis presented in Ref. [7] clearly indicate significant ionic bonding between Ni and H and weak metallic bonding between H–H atoms. The calculated valence charge density distribution in LaNiInH_{1.333} indicate that the Ni and H atoms form a NiH₂-molecule-like structural subunit and there is no substantial charge density between the H atoms [7].

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