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# Electronic structure and stability of hydrides of intermetallic compounds

M. Gupta\*

Laboratoire d'Etudes des Matériaux Hors Equilibre, Institut des Sciences des Matériaux, Bâtiment 415, Université de Paris-Sud, 91405 Orsay, France

## Abstract

We have investigated the electronic structure of several intermetallic compounds of AB and AB<sub>5</sub> type and their hydrides using the ab initio self-consistent linear muffin-tin orbitals method. The energy bands, total densities of states as well as their site and partial wave contributions are used to discuss the metal–hydrogen bonding features, the modifications of the electronic states at the Fermi energy on hydrogen absorption and the factors which control the stability. The specific systems investigated are zirconium-based AB compounds (A=Zr, B=Co, Ni) and their hydrides ABH and ABH<sub>3</sub>. We also discuss the effect of substitution at the Ni site in LaNi<sub>5</sub> by several elements of the 3d series (Mn, Fe, Co). In Zr-based AB hydrides, the Zr–H bonding contribution is crucial to the stability of the system due to the lowering of the energy states below the Fermi energy. The total energies of ZrNiH calculated for different site occupancies by the H atoms are in agreement with experimental trends. For the intermetallic compounds LaNi<sub>4</sub>M (M=Mn, Fe, Co) the Fermi level is found to lie in a narrow M-3d sub-band above the Ni-d states, and the densities of states are high. The lattice expansion accounts for less than 50% of the decrease in the stability, indicating the importance of the chemical substitution effects, besides the lattice expansion contribution. For the Co-substituted compound, the (3g) sites are found to be more stable than the (2c) sites, in agreement with experimental observations, and the maximum hydrogen content of the hydride LaNi<sub>4</sub>CoH<sub>4</sub> appears to be associated with the filling of the Co-d peak. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Electronic structure; Stability of hydrides; ZrNi-hydride; ZrCo-hydrides; La(NiM)<sub>5</sub> hydrides

## 1. Introduction

ZrNi is the first intermetallic compound which was found in the late fifties by Libowitz et al. [1] to reversibly absorb hydrogen, thus opening a new field of investigation, while ZrCo has been considered in the last fifteen years as a possible substitute for uranium for the storage of hydrogen and its isotopes, in particular tritium. The thermodynamic properties of these systems are of great interest to further improve the tritium storage conditions particularly to decrease the temperature of tritium recovery. In spite of this experimental interest, theoretical studies of the electronic structure and stability of these systems are still lacking.

A large number of experimental investigations on LaNi<sub>5</sub> and related compounds have been performed since the early 70's in relation to their exceptional hydriding properties [2,3]. Substitutions at the La or Ni sites are used to

modify the thermodynamic properties and play an important role in the selection of these alloys for specific technological applications, since they affect the stability and the hydrogen content of the hydride [4–7]. In order to optimize the choice of the intermetallic compound for a selected application, a better understanding of the role of each alloy constituent on the electronic properties of the material is crucial. Several semi-empirical models [8,9] have been proposed for the heat of formation and heat of solution of metal hydrides and attempts have been made for justifying the maximum hydrogen absorption capacity of the metallic matrices. These models show that the energetics of the metal–hydrogen interaction depend both on geometric and electronic factors. Up to date, however theoretical ab-initio studies of hydrides of complex systems are rather limited and cannot yet provide an answer to these interesting questions. In this paper we present some results of our attempt to a better understanding of hydrides of ZrNi, ZrCo, and ternary intermetallic compounds obtained from LaNi<sub>5</sub> by substitution of Ni by a 3d element. We briefly outline the computational method before presenting the theoretical results in light of experimental data.

\*Corresponding author.

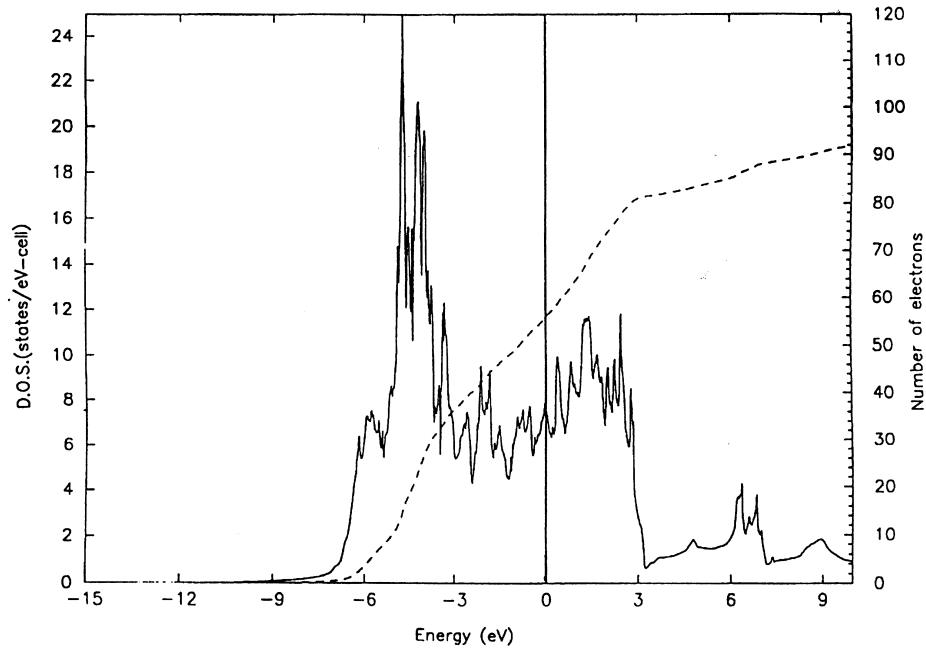


Fig. 1. Total DOS of ZrNi (full line) and number of electrons (dotted line).  $E_F$  is the origin of energies.

## 2. Computational method

The band structure calculations have been performed using the density functional theory (DFT) in the local density approximation (LDA). We have used the self-consistent linear muffin-tin orbitals (LMTO) method within the atomic sphere approximation (ASA), and the so-called combined correction terms were included to account for the overlap of the atomic spheres. The von Barth-Hedin approach was used to determine the exchange and correlation term of the crystal potential. The densities of states were calculated in a 1-mRy mesh with the linear energy tetrahedron method.

## 3. Results and discussion

### 3.1. $AB$ ( $A=Zr$ , $B=Ni,Co$ ) intermetallic compounds and their hydrides

The maximum hydrogen absorption in ZrNi and ZrCo leads to the formation of the isostructural hydrides ZrNiH<sub>3</sub> and ZrCoH<sub>3</sub>. From X-ray [10] and neutron diffraction experiments [11,12] the structure of the metal sublattice was found to be CrB-type orthorhombic (space group *Cmcm*). In the unit cell which contains four formula units, the H(D) atoms occupy pyramidal Zr<sub>3</sub>B<sub>2</sub> (4c), and tetrahedral Zr<sub>3</sub>B (8f) sites, a site occupancy consistent with neutron vibrational spectroscopy [13]. Thus for ZrNi which crystallizes also in the CrB-type orthorhombic structure, the hydride phase ZrNiH<sub>3</sub> corresponds essentially to a volume expansion of 20%. In contrast, ZrCo crystallizes in the cubic CsCl structure and the hydride phase ZrCoH<sub>3</sub> is thus associated with a structural change

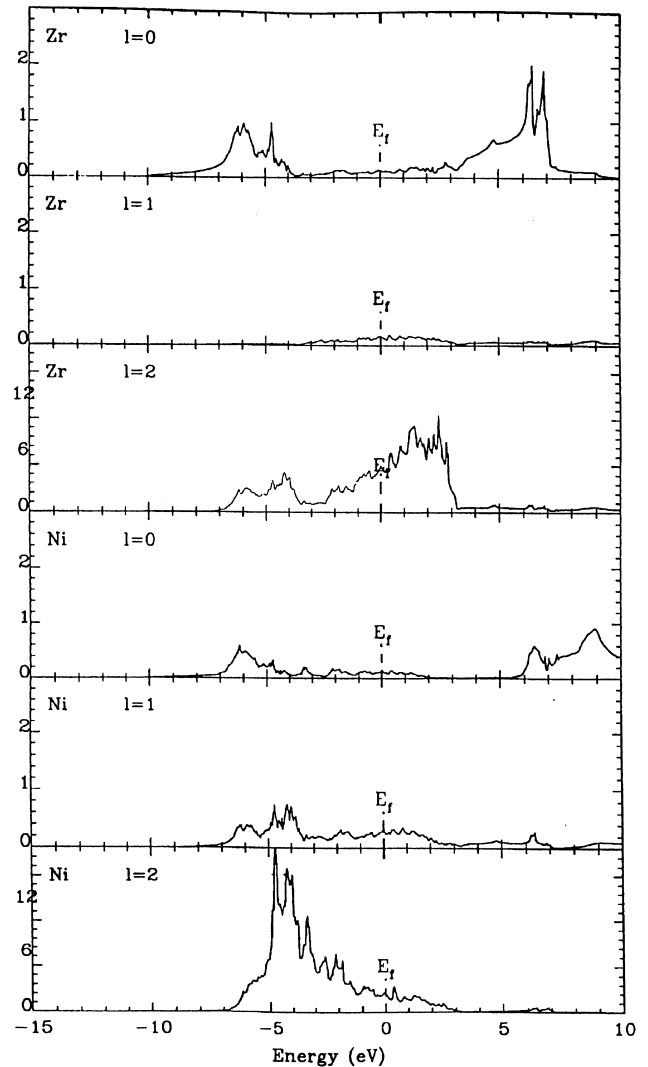


Fig. 2. Site and partial wave analysis of the DOS of ZrNi.

of the metal lattice, in addition to a volume expansion of 21.7%.

In order to analyze the atomic interactions between the two types of atoms, the total densities of states (DOS) of ZrNi plotted in Fig. 1 has been further decomposed in Fig. 2 into its partial wave (s, p, d) components around the two atomic sites. The major contribution of the Ni-d states is found at low energies, the main peak corresponds to rather localized states of width 3 eV situated between 3 and 6 eV below the Fermi energy  $E_F$ , while the main contribution of the Zr-d states, which are more delocalized, result in a broad structure of total width 6 eV located at higher energies between  $-3$  and  $3$  eV from  $E_F$ . The Zr 4d and Ni 3d states are of course strongly mixed as shown in Fig. 2, and hybridized with metal s,p states. The calculated total DOS at  $E_F$  is  $N(E_F)=1.89$  states per eV formula unit. The contribution of the Zr states at  $E_F$  represents 68% of the total, and is thus larger than of the Ni states. These features are in agreement with photoemission results on the NiZr system [14] which show clearly two separate structures due to Ni 3d at low energies and Zr 4d at higher energies close to  $E_F$  and the value of  $N(E_F)$  is compatible with magnetic susceptibility and low temperature specific heat measurements [15].

The total and partial wave analyses of ZrNiH<sub>3</sub> are plotted separately in Figs. 3–5. A comparison with the pure intermetallic compound reveals the following essential modifications: (1) On the low energy side a new structure associated with metal–hydrogen bonding and H–H interactions appears in the hydride between 4 and 13 eV below  $E_F$ ; (2) The energy separation between the Ni 3d and the Zr 4d main peaks decreases from the intermetallic to the hydride due to the lattice expansion, and the Zr 4d

DOS has been considerably modified by the presence of hydrogen; (3) The Fermi energy of the hydride is closer to the main Ni 3d peak. The observed lowering of  $E_F$  is associated mostly with the lattice expansion, and also with the Zr–H interaction effects which lead to an important lowering of the Zr 4d states located above the Fermi level in the pure intermetallic, a factor which is important for the stability of the hydride. The contribution of the Ni 3d states to the metal–hydrogen bonding is sizeable although it is lower than that of the Zr 4d states. This is due to the larger coordination number of H with Zr both in the pyramidal (Zr<sub>3</sub>Ni<sub>2</sub>) and the tetrahedral (Zr<sub>3</sub>Ni) sites. The most important difference observed in the bonding of H with Ni and Zr is that the Ni-d states were already occupied in the pure intermetallic while a majority of the Zr-d states were located above  $E_F$ ; this feature has important consequences on the Fermi energy position in the hydride. The total DOS decreases slightly in ZrNiH<sub>3</sub> to 1.83 states per eV formula unit; the Zr-d contribution at  $E_F$  decreases from 68% in the intermetallic to 62% in the hydride due to the broadening of the Zr states and the shift in  $E_F$ .

The main differences between the DOS of isostructural compounds ZrCoH<sub>3</sub> and ZrNiH<sub>3</sub> can be summarized briefly as follows: the Co 3d structure is broader and located at higher energies than the Ni 3d peak; the overlap with the Zr 4d states is larger in ZrCoH<sub>3</sub>. The Fermi level is closer to the Co-d peak since the electron count decreases by one per formula unit. The total DOS at  $E_F$  of ZrCoH<sub>3</sub> is rather large; it increases from 1.88 states per eV formula unit in the CsCl structure ZrCo to 2.44 states per eV formula unit in ZrCoH<sub>3</sub>. This indicates the possibility of antiferromagnetic behavior which has been mentioned

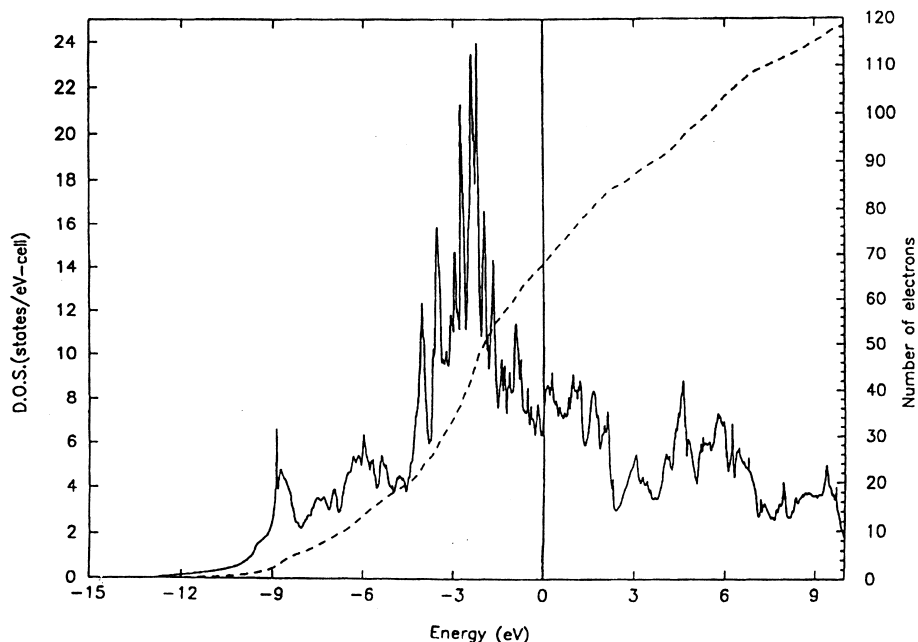


Fig. 3. Total DOS of ZrNiH<sub>3</sub> (full line) and number of electrons (dotted line).  $E_F$  is the origin of energies.

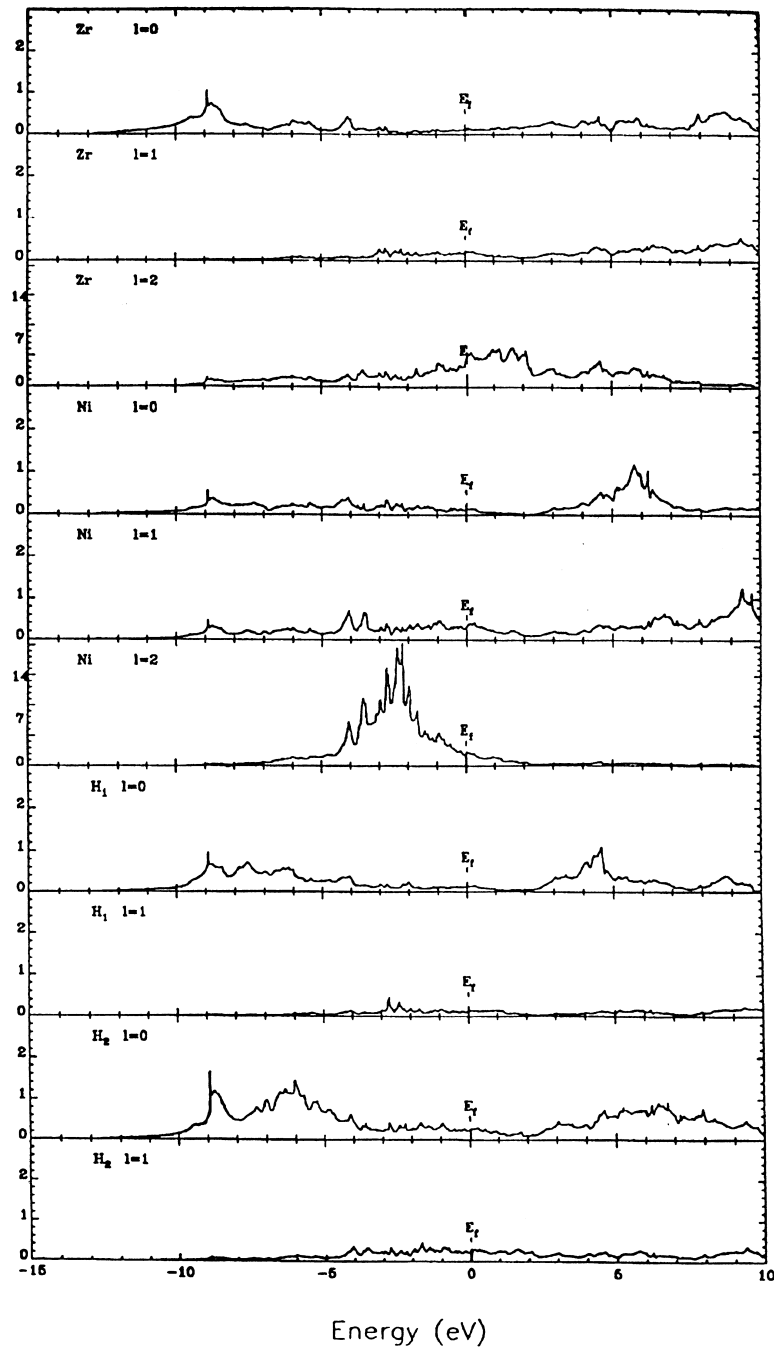


Fig. 4. Sites and partial wave analysis of the DOS of  $\text{ZrNiH}_3$ ;  $\text{H}_1$  and  $\text{H}_2$  atoms occupy respectively the (4c) and (8f) sites.

by Irodova et al. [12]. In  $\text{ZrCoH}_3$  the metal–hydrogen bonding states are centered at around 7 eV below  $E_F$ , in agreement with photoemission data [16].

We have also investigated the electronic structure of the stable compound  $\text{ZrNiH}$  using the structural data of Westlake et al. [17] in the  $Cmcm$  symmetry, an assumption justified because the observed triclinic distortion is not too large. In  $\text{ZrNiH}$ , the H(D) atoms occupy  $\text{Zr}_4$  (4c) sites which are different from those occupied in  $\text{ZrNiH}_3$ . The total and partial DOSs of  $\text{ZrNiH}$  are plotted in Figs. 6 and 7 respectively. In contrast to the results obtained for

$\text{ZrNiH}_3$ , the low energy metal–hydrogen bonding states in  $\text{ZrNiH}$  are largely dominated by the H–Zr contribution. A comparison of the position of the Fermi energy shows that  $E_F$  is closer to the Ni-d peak in  $\text{ZrNiH}$  than in  $\text{ZrNiH}_3$ . These two features are associated with an important energy lowering of the empty Zr-d states, which is crucial to the stability of  $\text{ZrNiH}$ . The origin of this lies in the local environment of the (4c) sites occupied in  $\text{ZrNiH}$ .

In the case of  $\text{ZrNiH}$  we compared the electronic structures obtained with different site occupancies for hydrogen atoms, namely, the  $\text{Zr}_4$  (4c) sites observed

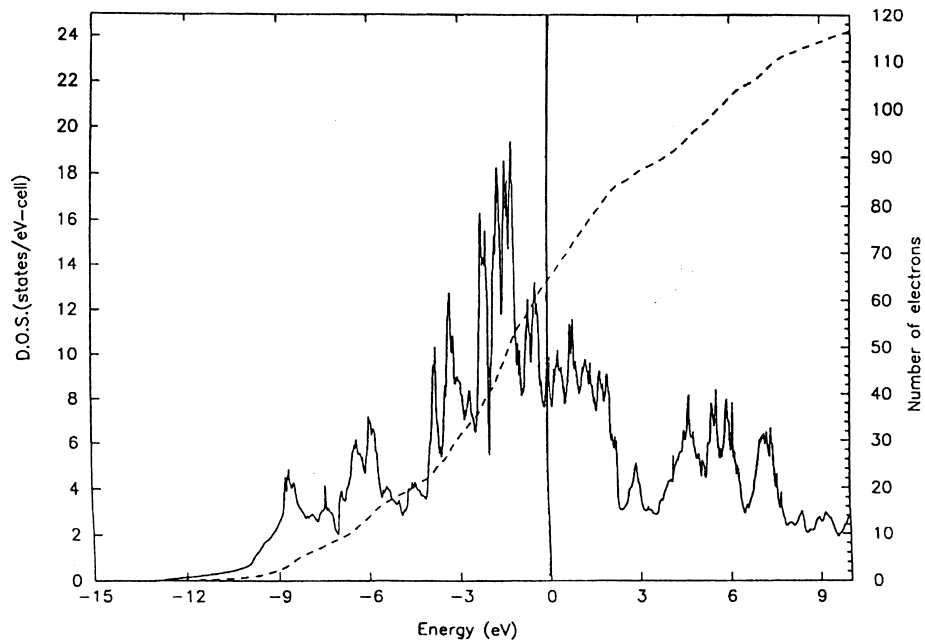


Fig. 5. Total DOS of  $\text{ZrCoH}_3$  (full line) and number of electrons (dotted line).  $E_F$  is the origin of energies.

experimentally and the  $\text{Zr}_3\text{Ni}_2$  (4c) sites which are occupied in the fully hydrogenated compound. We found that at a constant volume, the total energy associated with the occupancy of the  $\text{Zr}_4$  (4c) sites is significantly lower due to the strength of the  $\text{Zr-H}$  interaction. This puts on a quantitative basis the predictions of Westlake which were based on considerations of the interstitial hole size and  $\text{H-H}$  distances [18].

### 3.2. $\text{LaNi}_5M$ ( $M=\text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ ) intermetallic compounds and their hydrides

$\text{LaNi}_5$  crystallizes in the hexagonal  $\text{CaCu}_5$  structure [19], space group  $P6/mmm$  in which the La atoms occupy the (1a) sites; there are two types of Ni atoms occupying respectively the (2c) sites in the basal lanthanum planes ( $z=0$ ), and the (3g) sites in the middle plane ( $z=c/2$ ).

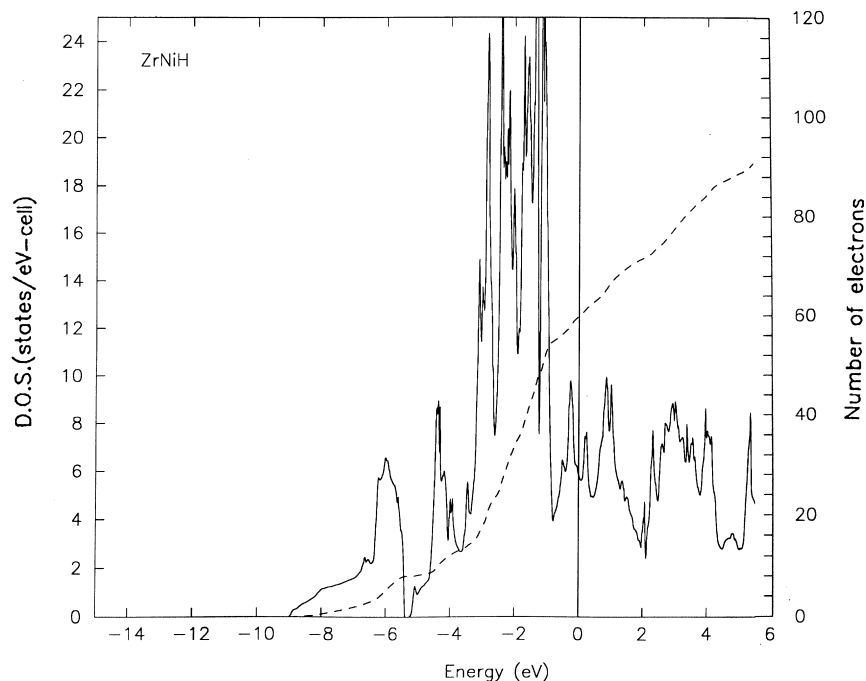


Fig. 6. Total DOS of  $\text{ZrNiH}$  (full line) and number of electrons (dotted line).  $E_F$  is the origin of energies.

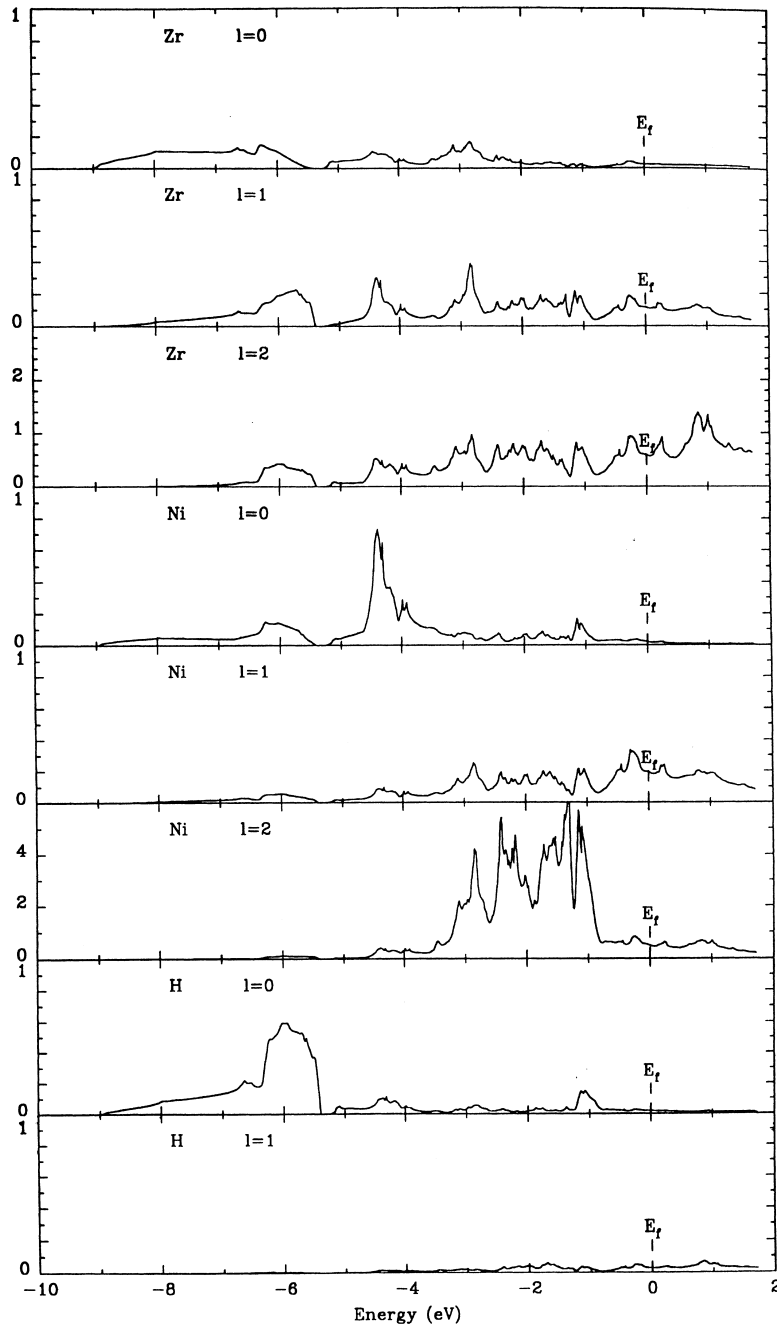


Fig. 7. Site and partial wave analysis of the DOS of ZrNiH.

Before discussing the effect of the substitutions at the Ni site on the electronic structure, we shall summarize the most salient features of the electronic structure of the reference compound  $\text{LaNi}_5$ . The total DOS of  $\text{LaNi}_5$  is plotted in Fig. 8. Its partial wave analysis around the different atomic sites, plotted in Fig. 9, shows that the occupied part of the conduction band is dominated by the Ni 3d states with a non negligible bonding contribution of the La-5d states. The main part of the La-5d states is located above the Fermi energy,  $E_F$ , chosen here as the origin of energies. The 4f La states are empty, they are

very localized, and give rise to a peak in the DOS centered around 3 eV above  $E_F$ . In agreement with our previous results using the tight-binding approximation in the recursion scheme [10], we find that the Ni-d bands are not filled in  $\text{LaNi}_5$ . The interaction of the La-5d with the Ni-3d states below  $E_F$  is large enough to lead to negligible charge transfer between La and Ni. In a simple model with a charge transfer of three electrons from La to Ni, since there are about 0.6 holes per atom in the Ni-d bands, one would have expected a complete filling of the Ni-d bands. Our theoretical results show that  $\text{LaNi}_5$  is not a charge transfer

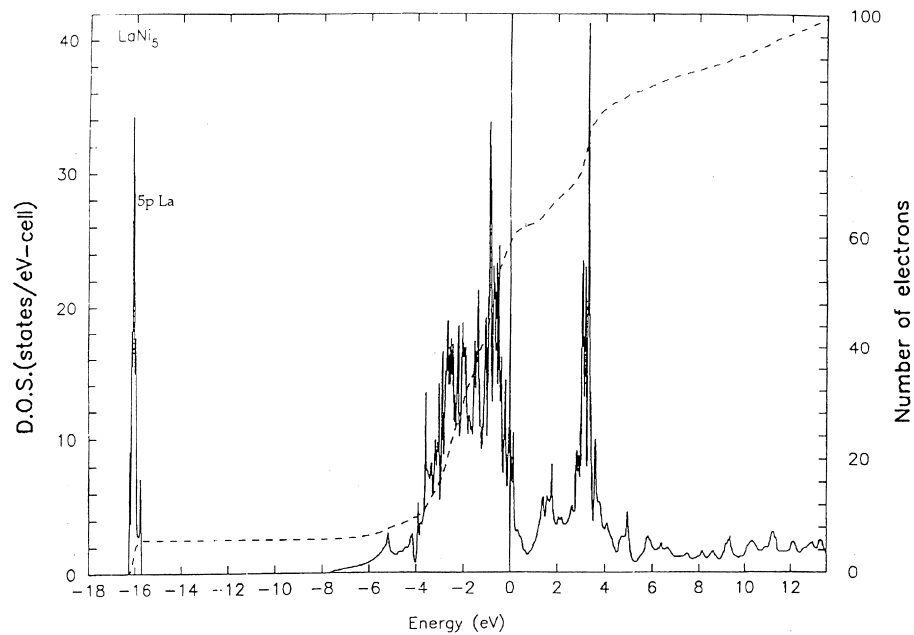


Fig. 8. Total DOS of  $\text{LaNi}_5$  (full line) and number of electrons (dotted line).  $E_F$  is the origin of energies.

compound and agree with the core level photoemission spectra of Schlapbach [16] which do not indicate any significant shift in the La-3d and Ni-2p core states in  $\text{LaNi}_5$ . The DOS at  $E_F$  is high and mostly composed of Ni-d states since the La-5d contribution is only 4%. This result is in general agreement with low temperature heat capacity measurements which lead to large values of the electronic specific heat coefficient  $\gamma=34.3 \text{ mJ} (\text{mol LaNi}_5)^{-1} \text{ K}^{-2}$  [4] and  $\gamma=42 \text{ mJ} (\text{mol LaNi}_5)^{-1} \text{ K}^{-2}$  [20] and with magnetic susceptibility data  $\chi=4.6 \times 10^{-6} \text{ emu g}^{-1}$  [21]. In spite of the large value of the DOS at  $E_F$ ,  $\text{LaNi}_5$  is a Pauli paramagnet. The calculated total DOS of  $\text{LaNi}_5$  shown in Fig. 8 is in good agreement with the XPS data of Fuggle et al. [22] concerning the width of the occupied states, and the high emission observed at  $E_F$  in  $\text{LaNi}_5$  as well as in pure Ni. Moreover, the satellite observed at  $-6 \text{ eV}$  below  $E_F$  in the Ni photoemission spectrum does not disappear in  $\text{LaNi}_5$ . Since this satellite is due to  $d^8$  final states effects, its presence in  $\text{LaNi}_5$  indicates that the Ni-d bands are not full.

Neutron scattering data [6,23] have shown that the substitutions at the Ni site by the 3d elements considered here occur predominantly at the Ni (3g) sites. We thus ignored for simplicity the partial, and generally small, occupancy of the (2c) sites as well as the disorder of the substituting elements by assuming an ordered array of the M atoms. In the case of  $\text{LaNi}_4\text{Co}$  we have also considered the Co substitution at the (2c) site which we found to be energetically unfavorable. Substitutions of Ni by neighbors, M, on the left of the periodic table ( $M=\text{Mn, Fe, Co}$ ) does not just lead to a simple depopulation of the Ni-3d bands. In all the substituted intermetallics a new narrow sub-band, associated with the 3d states of the element M,

appears slightly above the Ni-d bands. As shown in Fig. 10, in the case of  $M=\text{Mn}$  this new sub-band of width 1 eV, is centered around 0.5 eV above the main Ni-d peak. The corresponding structure is narrower and closer in energy to the Ni-d peak for  $M=\text{Fe}$  and  $\text{Co}$  as shown in Figs. 11 and 12. The lattice expansion associated with the Ni substitution results also in a narrowing of the Ni-d bands due to a decrease in the Ni-Ni interaction. The Fermi level of the substituted intermetallic falls in all cases in the narrow antibonding sub-band of the M element while the Ni-3d, M-3d main bonding structure is filled. As a consequence, the DOS at the Fermi level increases further from  $\text{LaNi}_5$  to  $\text{LaNi}_4\text{M}$ . This indicates, in agreement with experimental observations, a tendency towards magnetic ordering as a function of increasing M/Ni concentration.

The heats of formation of the substituted alloys  $\text{LaNi}_4\text{M}$  ( $M=\text{Mn, Fe, Co, Cu}$ ) have been measured by calorimetric methods [7]. In all cases, the substituted intermetallics are less stable than  $\text{LaNi}_5$ . Since these substitutions are accompanied by a volume increase, we have examined the role played by the lattice expansion in the decrease of the stability by performing total energy calculations for  $\text{LaNi}_5$  at the lattice parameters of the substituted compound. Using the lattice expansion of 5.3% observed between  $\text{LaNi}_5$  and  $\text{LaNi}_4\text{Mn}$  we found that this volume increase leads to a destabilisation of  $\text{LaNi}_5$  by only  $7.86 \text{ kJ mol}^{-1}$  which represents only 31% of the experimental difference between the enthalpy of formation  $\Delta H_f = -158.9 \text{ kJ mol}^{-1}$   $\text{LaNi}_5$  and  $\Delta H_f = -133.9 \text{ kJ mol}^{-1}$   $\text{LaNi}_4\text{Mn}$ . Thus the decohesion associated with the lattice expansion which leads to a narrowing of the Ni-d bands is not the main source of the decreased stability observed in the alloy. The remainder is due to pure chemical effects associated with

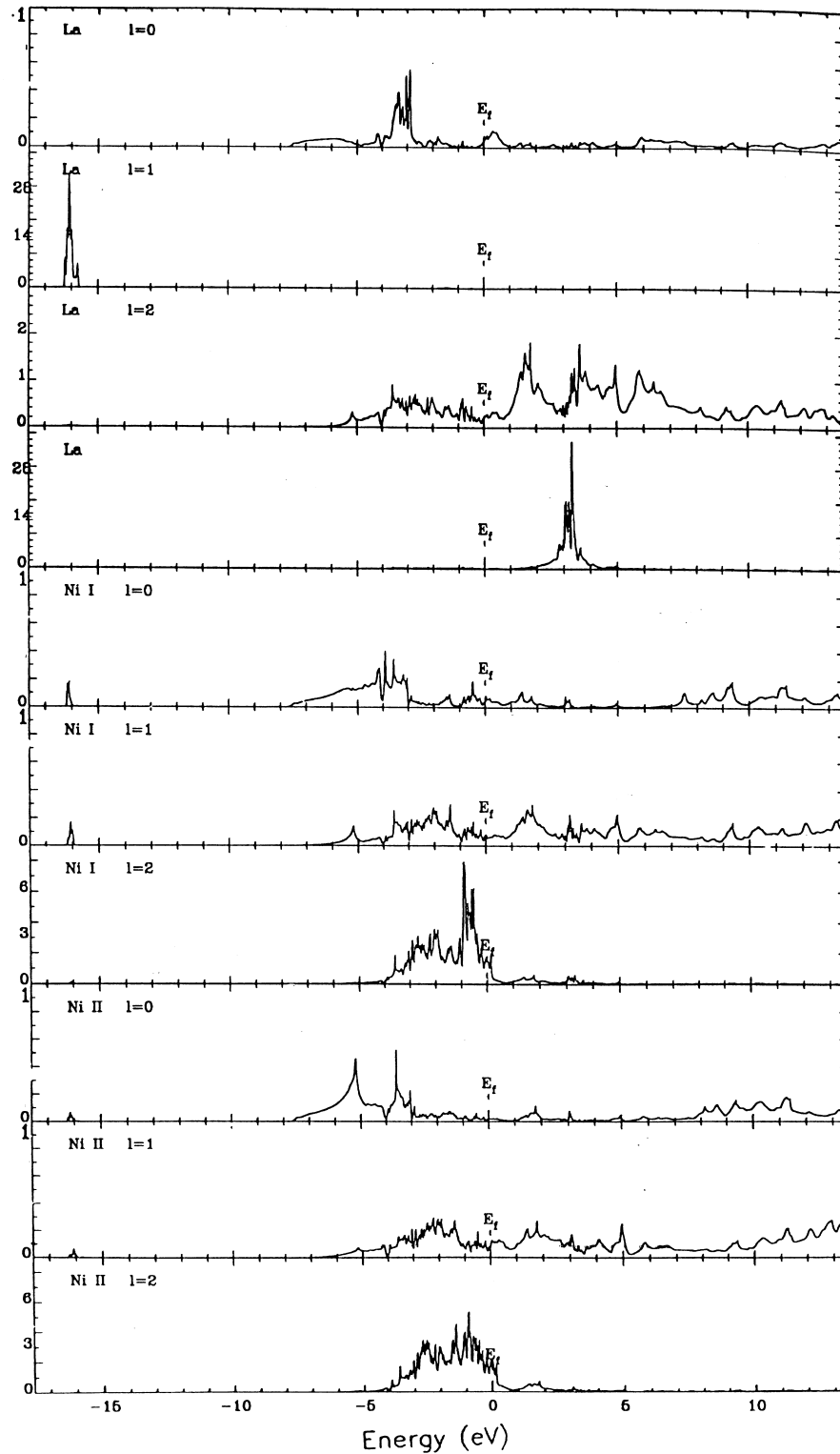


Fig. 9. Site and partial wave analysis of the DOS of  $\text{LaNi}_5$ . Ni I and Ni II atoms occupy respectively the (2c) and (3g) sites.

the presence of a new 3d sub-band, the filling of the main Ni-d structure and the shift in the Fermi level position. We have obtained similar conclusions for the other 3d-substituting elements.

We have also investigated the electronic structure of the

hydrides of the substituted intermetallic compounds. In Fig. 13 we have plotted the total DOS of  $\text{LaNi}_4\text{CoH}_4$ . In the calculation, we have used the neutron diffraction data of Gurewitz et al. [24] which shows that the deuteride belongs to the orthorhombic space group  $D_{2h}^{19}-C_{mmm}$  in



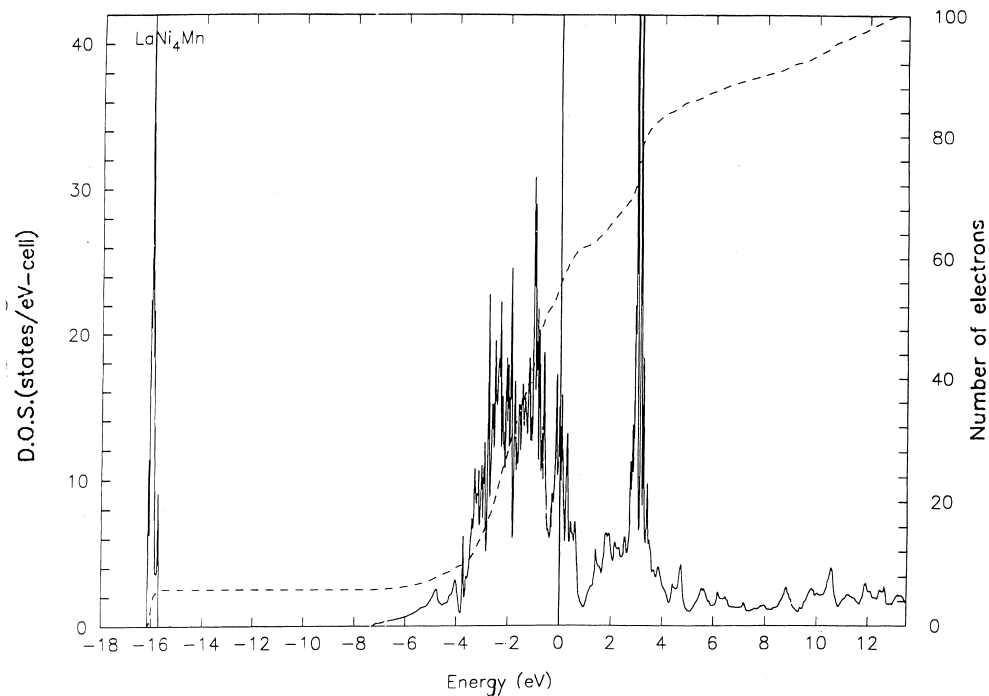


Fig. 10. Total DOS of  $\text{LaNi}_4\text{Mn}$  (full line) and number of electrons (dotted line).  $E_F$  is the origin of energies.

which  $D$  occupies the  $\text{La}_2\text{Ni}_4$  (4e) and  $\text{La}_2\text{Ni}_2$  (4h) sites of the structure. The main differences between the electronic structure of the intermetallic and its hydride can be briefly summarized as follows: (1) An additional structure in the DOS of the hydride is observed between  $-5$  and  $-10$  eV

which is due to metal–hydrogen bonding and H–H interactions. In this energy range, the La-d contribution to the La–H bonding is similar to that of the Ni-d, H-s interaction per nickel atom. The Co-d contribution to the bonding is smaller than that of Ni and occurs at higher

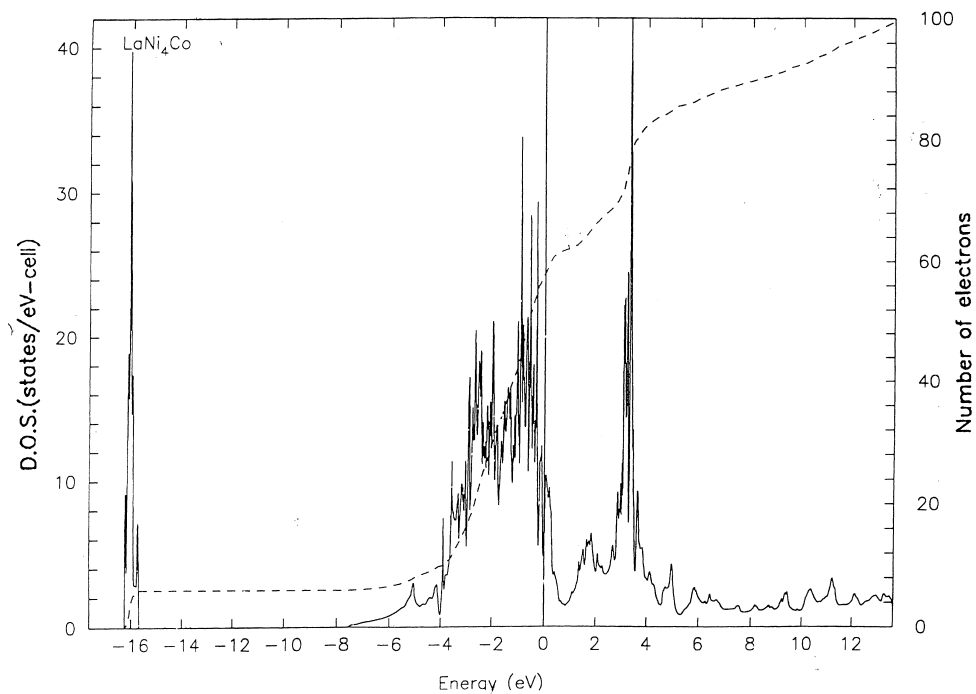


Fig. 11. Total DOS of  $\text{LaNi}_4\text{Co}$  (full line) and number of electrons (dotted line).  $E_F$  is the origin of energies.

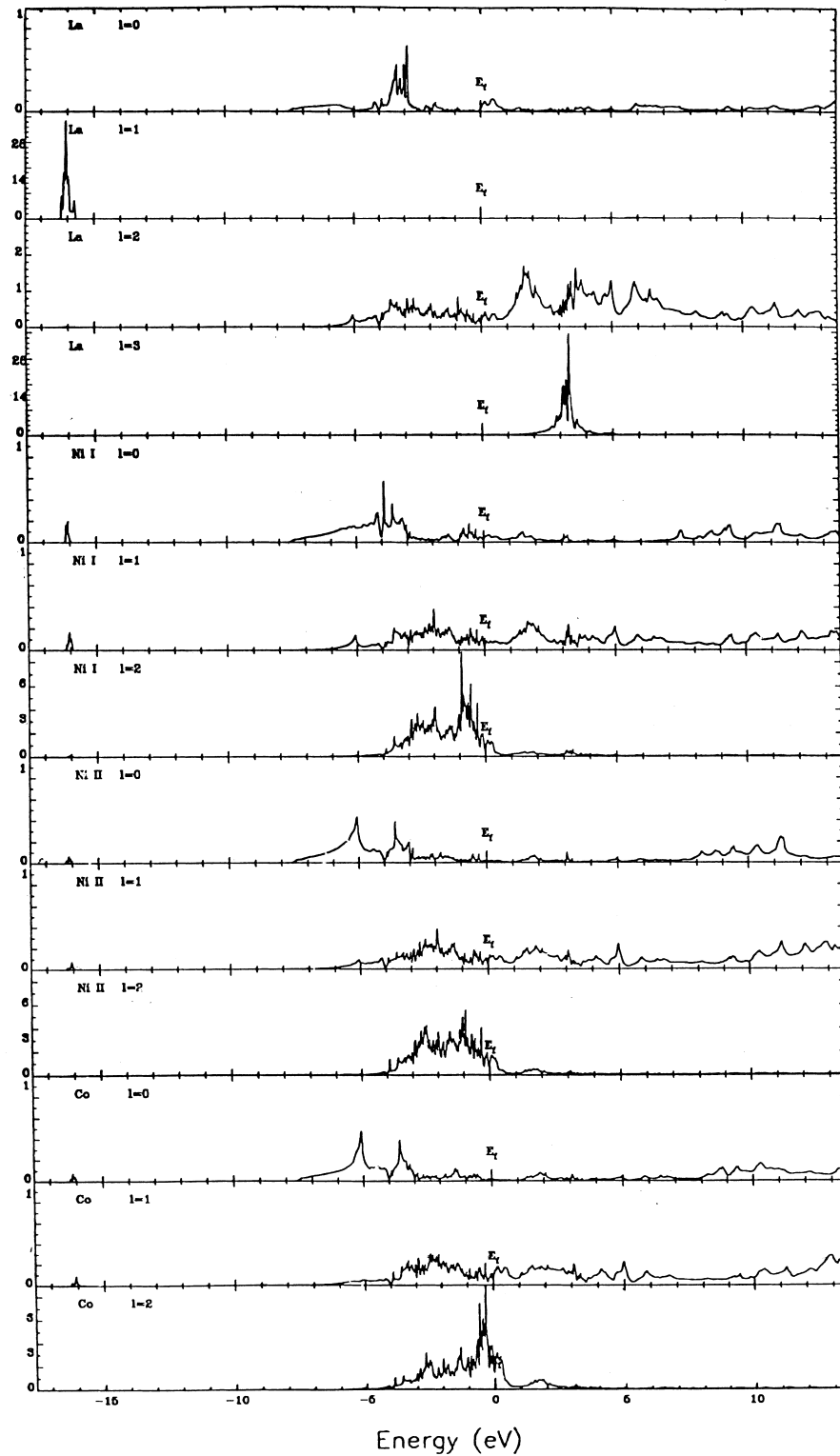


Fig. 12. Site and partial wave analysis of the DOS of LaNi<sub>4</sub>Co.

energies, above  $-6$  eV; these atoms interact mostly with the H atoms located at the (4h) sites; (2) The Fermi energy of the hydride falls in the valley of the DOS which separates the transition metal 3d states from the La 5d

states and the value of  $N(E_F)$  decreases from the intermetallic to the hydride. Clearly, the Fermi level of the hydride is higher than in the intermetallic since it corresponds to a filling of the main Co 3d peak. However, the

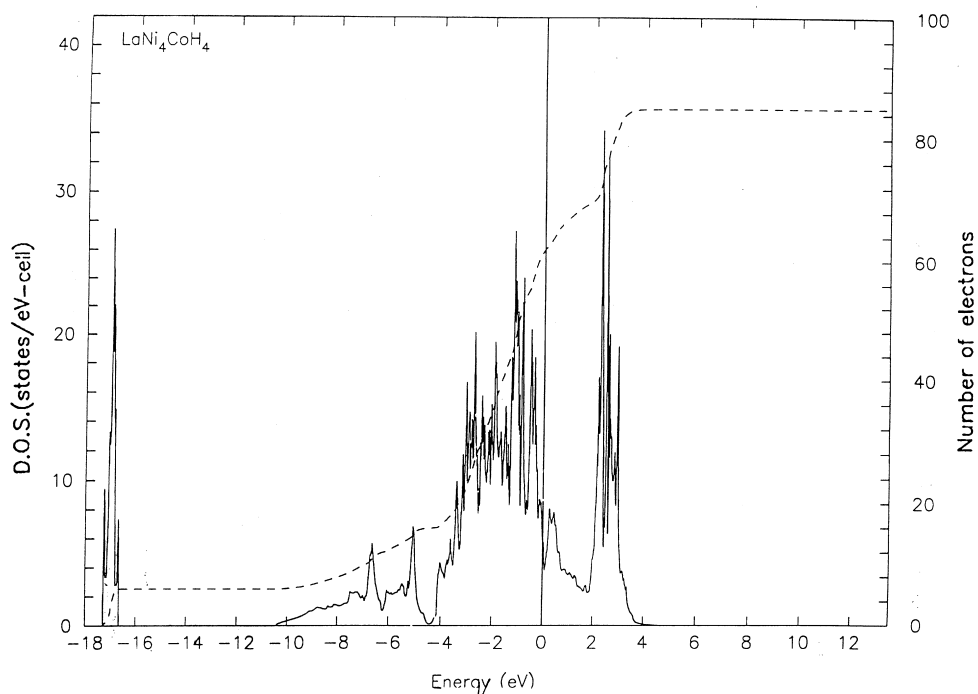


Fig. 13. Total DOS of  $\text{LaNi}_4\text{CoH}_4$  (full line) and number of electrons (dotted line).  $E_F$  is the origin of energies.

shift in  $E_F$  does not correspond to a filling of the bands in a rigid band model since the transition metal d states are substantially modified by the metal–hydrogen interactions.

In the hydride  $\text{LaNi}_4\text{CoH}_4$ , the maximum hydrogen content appears to be associated with the filling of the Co-d peak. Further shift of the Fermi energy would cost energy since the DOS is not too high.

#### 4. Conclusions

In the hydrides of ZrNi and ZrCo, the H–Zr interactions play a major role in the stability of the system since they create additional states below the Fermi level. These interactions depend strongly on the local environment and play an important role in the hydrogen site occupancy.

The substitution of Ni in  $\text{LaNi}_5$  by a 3d element leads to important modifications of the electronic structure of the intermetallic. In  $\text{LaNi}_4\text{M}$  (M=Fe, Co, Mn) the main Ni-d structure of the DOS is filled and the Fermi energy falls in the narrow additional M-3d sub-band located above the Ni-d states in a region of high DOS. We show that the effect of chemical substitution plays an important role in the observed decreased stability of  $\text{LaNi}_4\text{M}$  compared to  $\text{LaNi}_5$  since the lattice expansion alone accounts for less than 50% of the decohesion of the alloy. The metal–hydrogen bonding interactions play a major role in the stability of the hydride. However the Fermi energy is always found to rise, a factor which affects adversely the stability. The maximum hydrogen content in  $\text{LaNi}_4\text{CoH}_4$  is related to the complete filling of the Co-3d sub-band.

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