# Electronic and magnetic properties of Pd-Ni multilayers: Study using density functional theory

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## ABSTRACT

Electronic and magnetic properties of Pd-Ni multilayers have been studied using VASP method in the framework of the density functional theory (DFT). The calculations performed for different configurations ($Pd_n/Ni_m(111)$), where $n$ Pd layers are piled up over $m$ Ni layers with $n = 0$ to 4 and $n+m = 4$), reveal that the important magnetic moment of Ni is significantly enhanced according as $n$ increases due to hybridization effects between Pd and Ni mostly localized at the interface. The results also indicate that the Pd atoms are strongly polarized in the studied systems when compared with the pure metal.

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## 1. Introduction

This work is part of a most general study that involves the influence of the magnetism in the 1,3-butadiene adsorption on the Pd-Ni systems. The Pd-Ni multilayers have been selected because Pd deposits on Ni(111) exhibit a striking catalytic efficiency towards butadiene hydrogenation [1]. Studies on Pd films supported over Ni(111) have shown that Pd atoms are electronically perturbed and that this perturbation alters their catalytic properties [2].

In the past, theoretical studies have been realized employing semiempirical methods and clusters to described the metallic systems [3] without a spin polarized level. Actually, it is well-known that when multilayers are produced by a periodic repetition in one dimension of a unit cell consisting of a small number of monolayers (ML) of ferromagnetic and non-ferromagnetic elements, hybridization effects, strain and reduced coordination numbers at the interfaces of multilayers modify the magnetic behavior with respect to the bulk. In addition, the non-ferromagnetic element acquires an induced magnetic moment [4,5]. The magnetic properties of multilayers depend essentially on the layer-dependent distribution of the magnetic moments of both elements.

Magnetic multilayers constitute a new class of materials exhibiting a rich variety of novel phenomena related to the artificial structure; i.e., the great number of interfaces produces the confinement of electrons in ultrathin layers. Basic research into magnetism has been refreshed since the manufacture and discovery of new magnetic materials as well as the use of previously known material but with unusual geometry [6–9].

At present, scarce theoretical work has emerged in the literature [10]. We can mention two references related with the magnetism in $Ni_{1-x}Pd_x$ [11] and $Ni_xPd_{1-x}$ [12] alloys. In the first one, ab initio calculations for both FCC and BCC $Ni_{1-x}Pd_x$ alloys and $Co_{1-x}Pd_x$ alloys ($x = 0.25$; 0.50; 0.75; 1.00) have been carried out. The authors found, except BCC $Ni_{1-x}Pd_x$ alloys, that the enhancement of the magnetic moments of ferromagnetic atoms becomes larger as the percentage of Pd in the alloys increases, whereas the spin polarization of Pd atoms shows less sensitive about the change. In the second one, the same authors confirm your earlier first-principles calculations [11] and report a result obtained in single-crystalline $Ni_xPd_{1-x}$ alloy grown on $Cu(001)/FeCu_3$ layer over $GaAs(001)$ substrate. The alloy shows ferromagnetism when $x \geq 0.25$ at room temperature and its average magnetic moment decreases as Pd content increases.

The main goal of this work is to study the dependence of the magnetic properties of Pd-Ni with respect to the thickness variation of the different multilayers. From a theoretical point of view, on the other hand, it is therefore important to investigate the consequences of interaction between Pd and various ferromagnetic elements, using the first principles calculations as well as the model calculations. We have studied the local magnetism of bimetallic systems, particularly when Pt is deposited on close packed surfaces of Co [13] and Ni [14].

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The organization of this work is as follows. In a first section we give a brief description of the theoretical method and the model employed. Afterwards, a section is devoted to analyze the magnetic properties of the systems. We end showing the density of states (DOS) curves and making the comparison with experimental data and other theoretical calculations.

## 2. Calculational details

The calculations were performed using Density Functional Theory (DFT). The corresponding Kohn-Sham equations were solved applying the *Vienna Ab-initio Simulation Program* (VASP) [15–17]. The exchange-correlation functional was treated according to the *Generalized Gradient Approximation* (GGA) in the parameterization of Perdew–Wang (PW91) [18,19]. In order to describe the electron–ion interaction we used ab initio all electron projector-augmented-wave potentials (PAW) [20,21]. A plane wave cutoff energy of 450 eV was used in all calculations. For all slab calculations, surface ($3 \times 3$) unit cells were hexagonal and a ($3 \times 3 \times 1$) Monkhorst–Pack grid [22], which corresponds to 5 irreducible k-points, was used for the Brillouin zone integration. In VASP, the structure optimization is conducted according to the Hellmann–Feynman forces as evaluated after the electronic iterations on each trial structure converges. The structure optimizations were stopped when the force on each ion became smaller than 10 meV/Å. In order to take into account the magnetic properties of the systems, the computations were performed at the spin-polarized level (SP). The electronic structure was analyzed in terms of *Density of Orbital States* (DOS).

For the calculations an FCC stacking layered structure was assumed. The (111) surfaces were simulated by periodically repeated slabs of atoms separated in $z$ direction by a vacuum region. Previous tests with slab models containing up to five atomic layers have shown that a slab with four layers provides converged results; the difference in the surface energy between four and five layer-slabs is about 0.005 eV. The width of the vacuum gap was optimized to avoid the interaction between slabs. For that purpose, we observed that a distance of ∼15 Å was sufficient. The substrates were modeled considering that Pd layers were pseudomorphically deposited on Ni layers. The configuration used for the multilayers were of the type Pd$_n$/Ni$_m$(111) where $n$ Pd layers are piled up over $m$ Ni layers ($n$ = 0–4 with $n+m$ = 4). The studied systems were: Ni bulk, Pd$_0$Ni$_4$ (pure Ni surface), Pd$_1$Ni$_3$, Pd$_2$Ni$_2$, Pd$_3$Ni$_1$, Pd$_4$Ni$_0$ (pure Pd surface) and Pd bulk. The lattice constants (a) for Pd and Ni metals obtained from the bulk calculations are shown in Table 1. For comparison, the experimental lattice constants and those obtained in another

theoretical work [23] are also listed. All calculated values are slightly larger than the corresponding experimental values; this behavior is usual when GGA is used. Previous works related with metallic surfaces, showed that GGA potential gives better properties, such as lattice constant, correct ground state and adsorbate binding than local density approach (LDA) [24–27]. Meanwhile, the optimized cell values used for the surface bimetallic systems and their respective multilayer relaxation ($\Delta d_{1-2}$ and $\Delta d_{2-3}$) for SP and NSP calculations are also given in Table 1. The interlayer distances are in agreement with experimental studies reported employing XPS, LEED an XPD for ultra-thin films of Pd and Ni deposited on Ni(111) and Pd(111) surfaces [28]. These NSP and SP results showed that the magnitudes and directions of the interlayer relaxations were almost maintained. For pure Pd and Ni surfaces, both interlayer distances were contracted, while for the other multilayer systems $\Delta d_{1-2}$ expansions were presented. When the contents of Pd monolayers increase, the $\Delta d_{2-3}$ interlayer distances go from contraction to expansion.

## 3. Results and discussion

### 3.1. Magnetic properties

The magnetism in the bimetallic systems was studied by calculating the magnetic moments for all these surfaces. To our knowledge, this is the first study where Pd$_n$/Ni$_m$(111) multilayers are modelled. Table 2 summarizes the calculated local magnetic moments $\mu$ (in $\mu_B$) per atom according to the position of the layers in the slab The number indicates the position of the atoms layer in the slab: 1 (surface), 2 (subsurface), 3 (medium) and 4 (base).

In case of pure Ni surface (Pd$_0$Ni$_4$), the result shows that it is ferromagnetic with an average magnetic moment that remains almost without changes and differs 3.1% from Ni bulk. Nevertheless, some variation of magnetic moment from surface to inside the slab was observed (∼10%). As it was expected the magnetic moment of the inner slabs converged to the bulk value. For pure Pd surface (Pd$_4$Ni$_0$), we obtain an average magnetic moment of −0.002 μB/at. The calculation indicates that it is paramagnetic in agreement with the known experimental fact. Considering that the electronic configuration of Pd in its atomic state has a filled d shell (4d$^{10}$5s$^0$), the magnetic moment is null.

**Table 1**
Lattice constants of Pd bulk, Ni bulk and Pd$_n$/Ni$_m$(111) surfaces, where $n$ Pd layers are piled up over $m$ Ni layers ($n$ = 0 to 4 with $n+m$ = 4). $\Delta d_{1-2}$ (%) and $\Delta d_{2-3}$ (%) correspond to the interlayer relaxation between surface-subsurface spacing and subsurface-substrate, respectively, obtained for SP (1st line) and NSP (2nd line) calculations.

|  | Ni bulk | Pd$_0$Ni$_4$ | Pd$_1$Ni$_3$ | Pd$_2$Ni$_2$ | Pd$_3$Ni$_1$ | Pd$_4$Ni$_0$ | Pd bulk |
|---|---|---|---|---|---|---|---|
| a (Å) | 3.52 |  |  |  |  |  | 3.95 |
|  | 3.53 [23] | 3.53 | 3.64 | 3.74 | 3.89 | 3.97 | 3.96 [23] |
|  | 3.524$^{exp}$ |  |  |  |  |  | 3.891$^{exp}$ |
| $\Delta d_{1-2}$ (%) SP | – | −1.10 | 4.00 | 11.00 | 3.00 | −0.40 | – |
| NSP |  | −1.00 | 4.00 | 10.60 | 3.10 | −0.20 |  |
| $\Delta d_{2-3}$ (%) SP | – | −0.20 | −7.50 | −1.80 | 3.00 | −1.40 | – |
| NSP |  | −0.60 | −7.90 | −1.30 | 3.00 | −1.10 |  |

**Table 2**
Magnetic moments (in $\mu_B$/atom) for each layer in the slab. The number indicates its position in the slab: 1 (surface), 2 (subsurface), 3 (medium) and 4 (base). The calculated magnetic moments corresponding to Ni stand out in italic. The values coming from experiments are also shown. $W_F$ corresponds to the work function values obtained in this work for SP (1st line) and NSP (2nd line) calculations.

| System | $\mu_1$ | $\mu_2$ | $\mu_3$ | $\mu_4$ | $\mu_{exp}$ ($\mu_B$) | $W_F$ (eV) VASP | Exp. |
|---|---|---|---|---|---|---|---|
| bulk Ni | *0.614* | – | – | – | 0.61 [34] | 5.10 | 5.2 [35] |
|  |  |  |  |  |  |  | 5.17 [36] |
| Pd$_0$Ni$_4$ | *0.564* | *0.625* | *0.627* | *0.565* |  | 5.13 | 5.35 [38] |
|  |  |  |  |  |  | 5.24 |  |
| Pd$_1$Ni$_3$ | 0.129 | *0.775* | *0.690* | *0.620* |  | 5.17 |  |
|  |  |  |  |  |  | 5.16 |  |
| Pd$_2$Ni$_2$ | 0.264 | 0.333 | *0.820* | *0.716* |  | 5.43 |  |
|  |  |  |  |  |  | 5.49 |  |
| Pd$_3$Ni$_1$ | 0.282 | 0.444 | 0.335 | *0.855* |  | 5.37 |  |
|  |  |  |  |  |  | 5.37 |  |
| Pd$_4$Ni$_0$ | −0.001 | 0.000 | 0.002 | −0.008 |  | 5.32 | 5.60 [38] |
|  |  |  |  |  |  | 5.32 |  |
| bulk Pd | 0.000 | – | – | – | – | 5.32 | 5.60 [37] |

However, when Pd is in the metallic state a strong s–d hybridization takes place producing the unfilled d band $4d^{10-\delta}5s^{\delta}$ ($\delta\sim0.6$) with fairly large density of states at Fermi energy, leading to a net atomic magnetic moment [29]. In these calculations, the Pd atomic configuration $4d^9 5s^1$ was used

Thus, it is interesting to investigate the spin polarization of Pd atoms as nonmagnetic element in the vicinity of ferromagnetic atoms (Fe, Co, Ni) and to search the possibility to drive the metallic Pd to a ferromagnetic state due to some proximity effects, as it was reported in experimental studies for Fe/Pd [30,31] and Co/Pd [32,33]. For that purpose, we have evaluated the magnetism of the Pd-Ni systems analyzing different multilayer arrangements (see Table 2). In case of Pd atoms, the magnetic moment increases gradually with the Pd thickness starting from 0.1 to 0.4 $\mu_B$ for the $Pd_1Ni_3$, $Pd_2Ni_2$ and $Pd_3Ni_1$ multilayer surfaces. In previous theoretical results, we found a similar tendency for the Pt/Ni(111) bimetallic system [14]. When the Ni atoms are analyzed, a marked induced magnetic moment is shown, which is in some layers even bigger than the pure Ni surface. Such phenomenon is noticeable on the Ni atoms at the interface, where the higher magnetic moment reached is $\mu_4 = 0.855\,\mu_B$ for the $Pd_3Ni_1$ slab, enhanced by 39% with respect to the Ni bulk value (0.614 $\mu_B$ this work and 0.61 $\mu_B$ experimental value [34]). It would indicate the band hybridization importance on the Ni and Pd magnetization as it will show in Fig. 2(a–c) (see next section). For the sake of these results, we remark that the thickness of the Pd layers could be reduced to increase the total magnetization of the sample. Conversely, the Pd layer thickness must be increased if a higher magnetic moment on Pd surface is required.

To compare our results with earlier theoretical and experimental studies [11,12], the variation of Pd and Ni average magnetic moments as a function of $Pd_n$ layers was plotted in Fig. 1. After the pseudomorphically growing of one, two or three Pd layers onto Ni(111), forming a chemically ordered multilayers, the magnetic moment of Ni is enhances progressively compared with the pure Ni metal, reaching an enhancement of 44% with respect to the pure Ni surface. On the other hand, the situation changes considerably for Pd. Noticed that all Pd atoms become spin polarized with only one monolayer of Pd onto Ni(111) surface. The Pd average atomic moment obtained for the $Pd_n/Ni_m$(111) systems increases slowly until the slab contains three Pd layers. From here on, the slope decrease abruptly (Fig. 1). Similar behavior was reported by

Tang et al. [12] for the experimental average atomic moment obtained at room temperature for single-crystalline $Ni_{x-1}Pd_x$ thin films ($0\le x\le1$). The alloy shows ferromagnetism when $x\ge0.25$ and its average magnetic moment decreases as Pd content increases from 0.59 $\mu B$ ($x = 1.00$) to 0.32 $\mu B$ ($x = 0.38$). Our results are in better agreement when are compared with calculations performed for the same research group [11]. In this theoretical study, comparable ferromagnetic behavior was obtained for FCC-$Ni_{x-1}Pd_x$ alloys and for our multilayer systems.

The last column of Table 2 compares the values for the work function ($W_F$) obtained using VASP (SP and NSP calculations) against the experimental results coming from references [35,36]. There are good agreements between experimental and calculated work functions for bulk systems, observing the higher variation for Pd ones (5%) [37]. In case of (111) surfaces, the discrepancy among SP and NSP levels became important for the Ni ferromagnetic metal. For pure Pd and Ni(111) surfaces, the work function are lower by approximately 0.25 eV compared with the respective experimental values [38]. However, we obtained almost the same values of the work functions for Ni(111) and Pd (111), with respect to earlier theoretical studies (5.11 and 5.24 eV, respectively) [39,40]. In all the cases, the work functions increase for bimetallic systems. The $Pd_1Ni_3$ slab has higher work function than the pure Ni(111) surface. This behavior is repeated in $Pd_3Ni_1$ system with respect to the pure Pd(111) surface. On the other hand, an increasing in the work functions is produced as Pd thickness increases up to $n = m$, i.e., the same proportion of Pd and Ni metals in the slab. Finally, the work function decreases for $Pd_3Ni_1$ with tendency toward the pure Pd(111) surface value. These results indicate that the extraction of an electron from the bulk to outside the surface is harder when the Pd surface is deposited pseudomorphically on Ni(111).

### 3.2. Electronic properties

Fig. 2(a–e) exhibit the DOS (up and down) curves corresponding to the total 3d band of Ni and 4d band of Pd for $Pd_1Ni_3$, $Pd_2Ni_2$ and $Pd_3Ni_1$ arrangements. The unbalance between the spin-up and the spin-down states is the reason behind the magnetism of these systems.

In all cases, the DOS curves corresponding to Pd atoms (Fig. 2(a–c)) show an enlargement of ~1 eV, when are compared with pure Pd(111) surface (see Fig. 2d). This valence band broadening is due to the reduction of Pd-Pd distance when metallic Pd are pseudomorphically deposited on Ni(111), i.e., a greater overlap between Pd atoms takes place. Therefore, this behavior is essentially related to a geometrical effect. Moreover, the number of states at Fermi level (d-DOS($E_F$)) up and down on $Pd_1Ni_3$, $Pd_2Ni_2$ and $Pd_3Ni_1$ are remarkably lower than on $Pd_4Ni_0$ system.

Nevertheless, the variations in the energy range covered by d-band for Pd overlayers are a consequence of: (1) a reduction in Pd-Pd distance that produces a broadening in the Pd d-band width and (2) changes in the Pd-substrate interactions that shift the centroid of the Pd d-band (−1.57 eV for Pd pure) toward higher binding energy (−1.86, −2.02 and −2.18 eV for $Pd_3Ni_1$, $Pd_2Ni_2$ and $Pd_1Ni_3$, respectively). These downshifts in energy suggest the electron transfers from Pd to Ni substrate. In these systems, the relative importance of both the structural and the chemical effects through the interactions between the two components should be recognized.

At the same time, the up and down density of states contributed only from the Ni atoms in $Pd_1Ni_3$, $Pd_2Ni_2$ and $Pd_3Ni_1$ are also provided in Fig. 2(a–c) to explain the dependence of the Ni magnetic moments with of composition. Particularly, we underline that the larger unbalance between the spin-up and
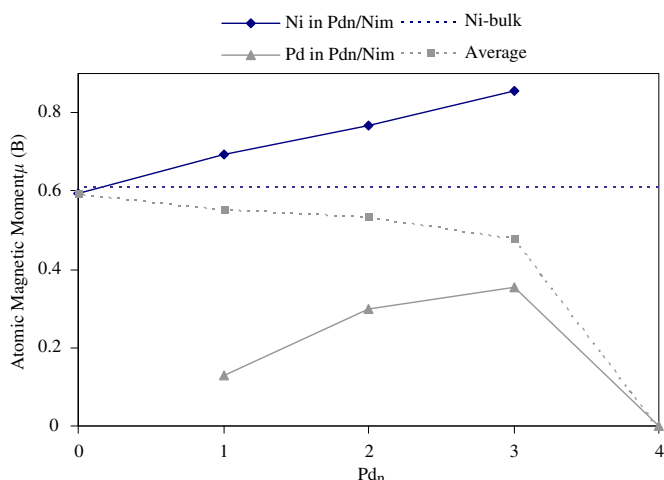


**Fig. 1.** Calculated magnetic moments obtained for the systems $Pd_0Ni_4$ (Ni pure), $Pd_1Ni_3$, $Pd_2Ni_2$, $Pd_3Ni_1$ and $Pd_4Ni_0$ (Pd pure). Moments of Ni and Pd are the averaged values per atom in unit cell. The average moment corresponds to the total magnetic moment in unit cell. The magnetic moment of Ni bulk is represented by a horizontal dotted line. The units are given in $\mu_B$/atom.
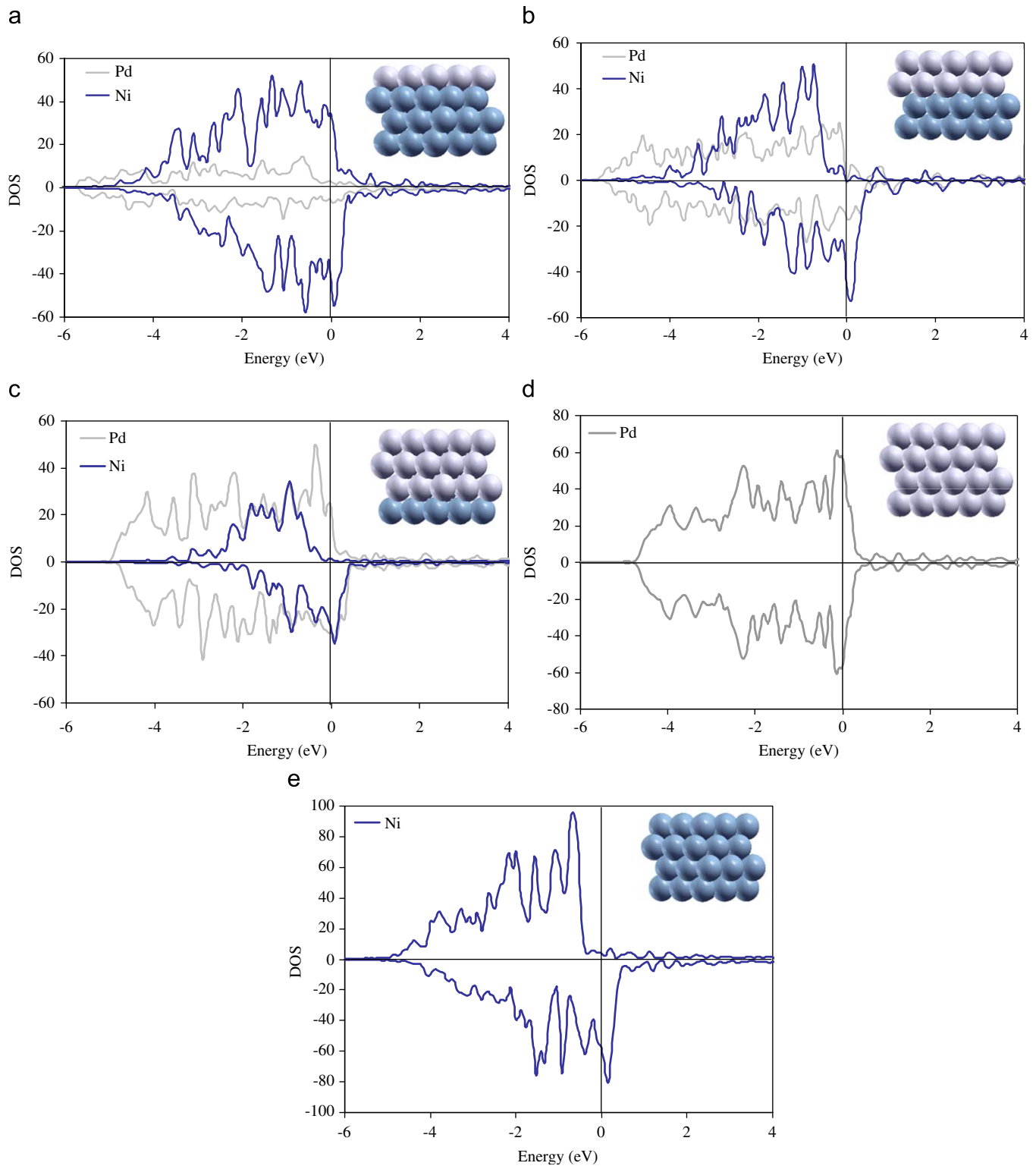
**Fig. 2.** Density of states (DOS) of the d-band obtained from a spin-polarized calculation for the systems (a) $Pd_1Ni_3$, (b) $Pd_2Ni_2$, (c) $Pd_3Ni_1$, (d) $Pd_4Ni_0$ and (e) $Pd_0Ni_4$. The origin of the energy scale corresponds to the Fermi level. The spin-down cases were plotted as negative values. The respective schematic representations of Pd-Ni(111) multilayers using slabs are at the top. The Ni monolayers are represented in blue and Pd ones in gray (color online).

the spin-down states of the Ni atoms present in $Pd_3Ni_1$ is in agreement with the magnetic moment enhancement of the Ni at the interface Pd-Ni, coming from the strong band hybridization.

For these systems, the hybridization effects and overlapping have a range within −4 and 0 eV. The relative importance of both, the structural and the chemical effects, through the interactions between the two components should be recognized.

## 4. Conclusions

A GGA-DFT study of the magnetic and electronic properties of $Pd_n/Ni_m(111)$ multilayer configurations, including Pd(111) and Ni(111) surfaces, was performed.

The magnetism was studied by calculating the magnetic moments per atom in each slab layer for all these surfaces. We

notice that the Pd surface atoms in the different bimetallic slabs have a magnetic moment which is enhanced from the Pd pure. On the interface, the non-ferromagnetic element acquires an induced magnetic moment nearly $0.3\,\mu_B$ increased with respect to pure Pd surface ($\sim 0\,\mu_B$), in a good concordance with previous experimental and theoretical results. A marked induced magnetic moment for Ni atoms, which in some layers is even bigger than that of the pure Ni surface, can be appreciated. Such phenomenon is noticeable on the magnetic moment of the Ni atoms at the interface for $Pd_2Ni_2$ slab which is enhanced by 34% with respect to the Ni bulk; the same effect can be appreciated for $Pd_3Ni_1$ slab (39%). These effects may be attributed to hybridization at the interfaces.

The work function values are in agreement with those obtained experimentally and increase for bimetallic systems. The electronic structure using the concepts of the density of orbital states was analyzed. The broader d-band for the Pd overlayer in comparison with pure Pd must be outlined. The DOS curves for the d-bands explain the phenomenon of magnetic induction in the multilayer configurations.

For the analyzed systems, the relative importance of structural and chemical effects through the interactions between the two components, should be recognized.

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