Volume 254, No. 1, 31 October 2007 ISSN 0169-4332

Available online at www.sciencedirect.com
ScienceDirect
Applied Surface Science 254 (2007) 355–359
applied surface science
www.elsevier.com/locate/apsusc

Structural and magnetic properties of Ni/Pt multilayers

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Available online 10 July 2007

Abstract

In this work, the variation of the magnetic moments of the Ni/Pt multilayers are studied using the linearized augmented plane waves (LAPW) method in the framework of the density functional theory (DFT) implemented in the version of WIEN2K program. The systems have been modeled by seven layers slab separated in z direction by a vacuum region of four substrate layers. We present the results of the dependence of the magnetic properties with respect to the thickness variation of the different multilayers. The modeling of these systems finds an important empirical support. Experiment and theory show the same trends for the magnetic moments: hybridization effects between Ni and Pt are mostly localized at the interface.

PACS : 75.70.Ak; 71.00.00

Keywords: Multilayers; *Ab initio* calculations; Ni/Pt

1. Introduction

Magnetic multilayers constitute a new class of materials exhibiting a rich variety of novel phenomena related to the artificial structure, the great number of interfaces and the confinement of electrons in ultra thin 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. Superlattices and metallic multilayer configurations have been studied for more than 70 years [1]. Despite the advance in vacuum technology, there has been no significant impact in the research of the magnetic properties until 1980s. Advances in experimental techniques with specific elements has recently allowed us to study the magnetism over thin magnetic films as well to get complete information in order to be contrasted with the theory.

The word superlattices was formerly used to name multilayer configurations with long range structural coherence along the growth direction [2]. These particular geometrical configurations are the ones that can modify the physical properties. Usually, multilayers are produced by a periodic repetition in one dimension of a unit cell consisting of a small number of monolayers (ML) of a ferromagnetic and a 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 [3,4]. The magnetic properties of multilayers depend essentially on the layer-dependent distribution of the magnetic moments of both elements.

The Ni/Pt multilayers have been selected because they have sharp interfaces in the ML limit and they are of technological importance as candidates for magneto-optic recording because of the presence of perpendicular magnetic anisotropy (PMA). In contrast with others systems, Ni/Pt multilayers present the PMA at room temperature when the non-magnetic layers (Pt) have very small thickness (2–3 Å) [5]. Shin et al. [6] reported magnetic perpendicular anisotropy in Ni/Pt multilayers, as well as their magnetic properties.

X-Ray magnetic circular dichroism (XMCD) experiments have been conducted in a group of Ni_n/Pt_m multilayer configurations with n and m between 2 and 13 monolayers, under 10 K fluorescence detector [4]. The respective electronic structure of these multilayer configurations has been theoretically calculated with an *ab initio* technique, specifically the tight-binding linearized muffin-tin orbital (TB-LMTO) method

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doi:10.1016/j.apsusc.2007.07.039

[4]. At present, the scarce theoretical work has emerged in the literature. The main goal of this work is to study the dependence of the magnetic properties with respect to the thickness variation of the different multilayers. In the past, we studied the local magnetism of bimetallic systems, particularly when Pt is deposited on close packed surfaces of Ni and Co [7].

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 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 exchange-correlation functional was treated according to the generalized gradient approximation (GGA) in the parameterization of PBE [8]. The corresponding Kohn–Sham equations were solved applying the full-potential linearized augmented plane-wave (FP-LAPW) method [9].

For the calculations an fcc(1 1 1) layered structure was assumed. The (1 1 1) surface was simulated by periodically repeated slabs of seven layers of atoms separated in z direction by a vacuum region. The width of this gap was optimized to avoid the interaction between slabs. For that purpose, we observed that a distance of four atomic layers was sufficient. The configuration used for the multilayers were of the type Ni_n/Pt_m(1 1 1) where nNi layers are piled up over mPt layers and so on. The studied systems were: bulk Ni, Ni_7Pt_0 (pure Ni surface; Fig. 1a), $(Ni_1Pt_1)_3Ni_1$ (Fig. 1b), $Ni_2Pt_3Ni_2$ (Fig. 1c), Ni_0Pt_7 (pure Pt surface; Fig. 1d) and bulk Pt. The lattice constants for Pt and Ni bulk were optimized obtaining 3.98 and 3.53 Å for Pt and Ni, respectively. Meanwhile, the cell values used for the surface bimetallic systems were: $a = b = 2.74$ Å ($(Ni_1Pt_1)_3Ni_1$) and $a = b = 2.82$ Å ($Ni_2Pt_3Ni_2$). The distances between successive planes Ni–Pt (2.23 Å) were adjusted employing their atomic radii.

The calculation parameters were optimized. In order to prevent overlap of the MT spheres the muffin-tin radius (R_{MT}) was fixed at 2.30 bohr for Ni and 2.60 bohr for Pt [7,10]. For the multilayers, the R_{MT} was fixed at 2.35 bohr for both metals. The LAPW wave functions within the muffin-tins were expanded in spherical harmonics with angular momenta up to $l_{max} = 10$ and a plane wave basis expansion in the interstitial region up to $|K_{max}|^2 = 14.7$ Ry. The (l, m) expansion for the potential goes up to $l_{max} = 4$. The cutoff energy for the Fourier-series expansions of the interstitial electron density and potential was $|G_{max}|^2 = 169$ Ry. The Brillouin zone integration was made using 30k points in all the multilayers cases and 20k points for bulk Pt and bulk Ni cases. In order to take into account the magnetic properties of Ni, the computations were performed at the spin-polarized level (sp). The electronic structure was analyzed in terms of local density of orbital states (LDOS).

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. Table 1

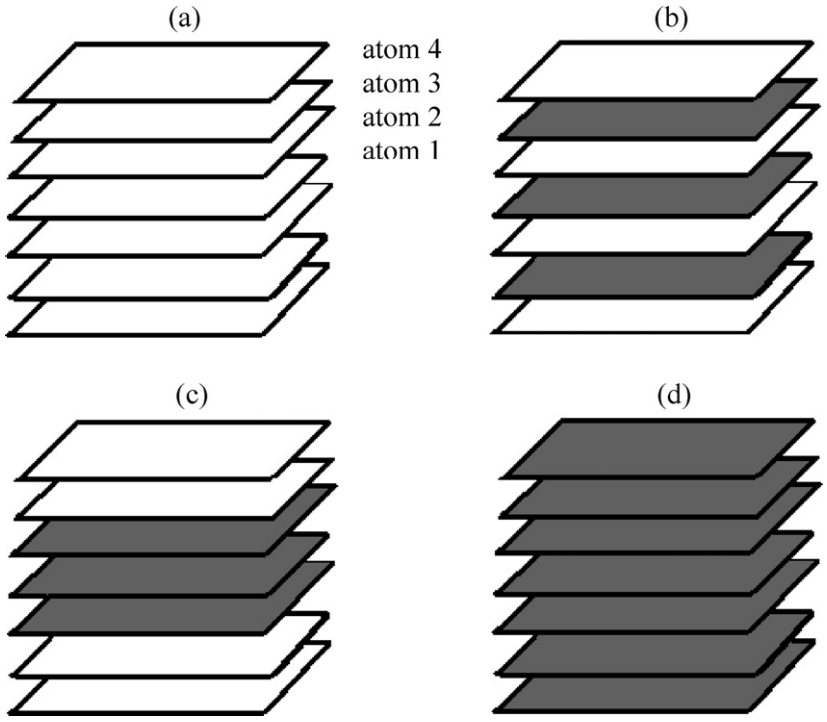

Fig. 1. Schematic representations of Ni/Pt(1 1 1) multilayers: (a) Ni_7Pt_0, (b) $(Ni_1Pt_1)_3Ni_1$, (c) $Ni_2Pt_3Ni_2$ and (d) Ni_0Pt_7. The atom number shows its position within the slab: 1 (center), 2 (medium), 3 (subsurface) and 4 (surface). The Ni monolayers are represented in white and Pt ones in gray.

Table 1
Magnetic moments (in μB/atom) for each non equivalent atom in the slab

System	μ_1 (μB)	μ_2 (μB)	μ_3 (μB)	μ_4 (μB)	μ_{exp} (μB)	W_F (eV)	
						LAPW	Exp.
Bulk Ni	0.606	–	–	–	0.61 [11]	–	
Ni_7Pt_0	0.662	0.673	0.709	0.712	–	5.044	5.2 [13]
$(Ni_1\ Pt_1)_3\ Ni_1$	0.223	0.860	0.252	0.882	–	4.941	–
$Ni_2\ Pt_3\ Ni_2$	0.232	0.281	0.833	0.818	–	4.676	–
$Ni_0\ Pt_7$	0.096	0.132	0.120	0.095	–	5.685	5.93 [14]
Bulk Pt	0.009	–	–	–	–	–	

The atom number indicates its position in the slab: 1 (center), 2 (medium), 3 (subsurface) and 4 (surface). The values coming from experiments are also shown. W_F corresponds to the work function values obtained in this work.

summarizes the calculated local magnetic moments μ (in μB/atom) for the different atoms of our slab models. The atom number indicates the position of the atom in the slab: 1 (center), 2 (medium), 3 (subsurface) and 4 (surface).

Firstly, notice that the magnetic moment for surface Ni atom (4), in system Ni_7Pt_0, differs from that of a Ni atom in the center (1): 0.71 μB in comparison with 0.66 μB. This is a well-known property due to the presence of surface states and band narrowing. However, the center Ni atom (1) presents μ similar to the bulk Ni; this is due to the used thickness ($n > 2$) [11]. All the multilayer arrangements have shown a marked induced μ, which in some layers is even bigger than that of the slab of pure Ni surface. Such phenomenon is noticeable on the surface Ni atom (4) where $\mu = 0.88$ μB for the $(Ni_1Pt_1)_3Ni_1$ slab, which is enhanced by 50% with respect to that of bulk Ni (0.61 μB). In Ref. [12], Choi et al. found for the 100%-Pt surface the same effect, with an increment of the 50% between the magnetic moment of the subsurface Ni atom (0.85 μB) and that of bulk Ni (0.58 μB). It shows the importance of band hybridization on the Ni and Pt magnetization. The same effect can be appreciated for $Ni_2Pt_3Ni_2$ slab (33.3%). In previous theoretical results [7] we found a similar tendency for the Pt/Ni(1 1 1) bimetallic system.

The multilayers systems ($(Ni_1Pt_1)_3Ni_1$ and $Ni_2Pt_3Ni_2$) show an induced μ in the Pt atoms improved by 50% with respect to that of pure Pt surface. The magnetic moment profile for the different slabs of Table 1 are shown in Fig. 2. This figure shows the magnetic moment per atom, according to the position of the layers in the slab.

Using XMCD, Wilhelm et al. [4] measured experimentally the magnetic moment per atom for a Ni_6/Pt_5 multilayer system, obtaining a magnetic moment of ≈ 0.29 (± 0.04) μB/atom at the Pt-interface while at the Ni-interface it is strongly reduced

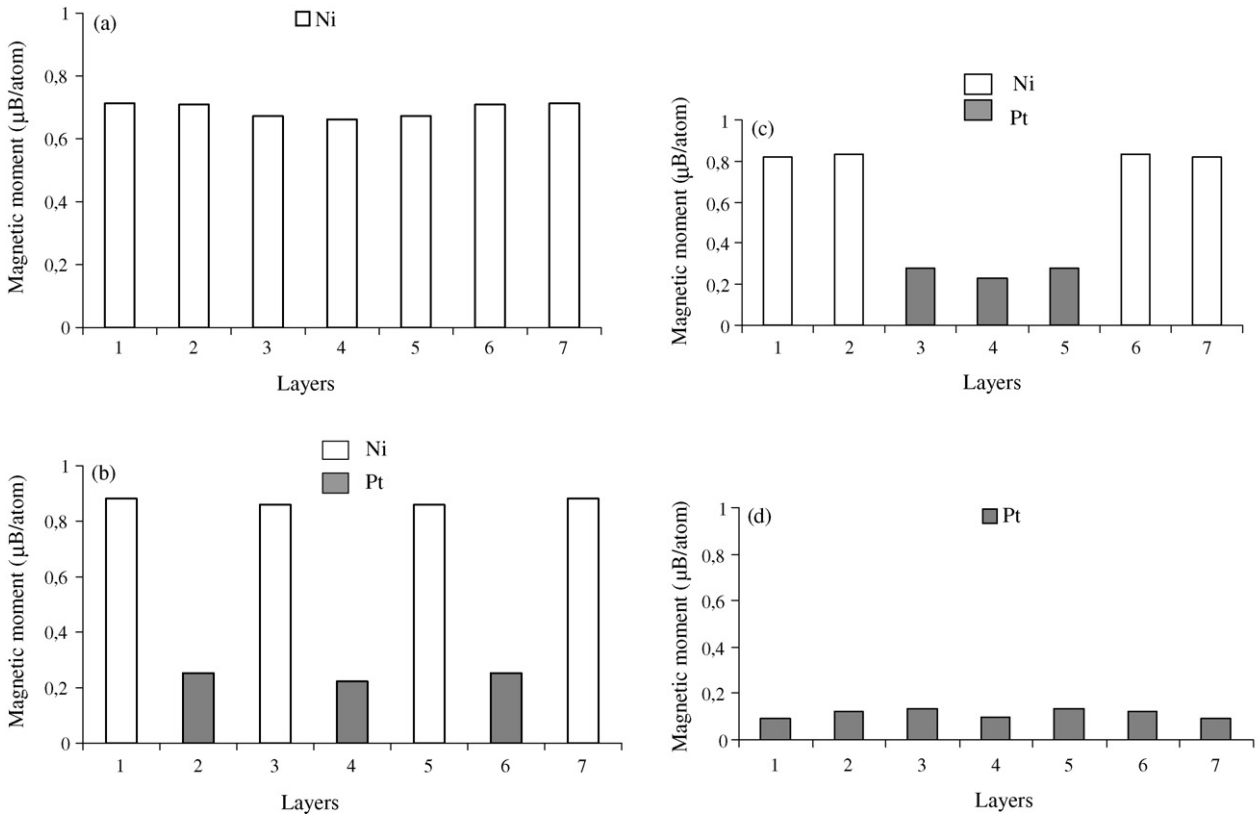

Fig. 2. Theoretical magnetic moment profile for the unit cell, obtained for the systems Ni_7Pt_0 (a), $(Ni_1Pt_1)_3Ni_1$ (b), $Ni_2Pt_3Ni_2$ (c) and Ni_0Pt_7 (d).

Table 2
Magnetic moments in the interface zone for $Ni_2Pt_3Ni_2$ system

Magnetic moment	XMCD exp. Ni_6/Pt_5	FP-LAPW Ni_2/Pt_3	TB-LMTO Ni_6/Pt_5
$\mu_{Pt\text{-}int}$ (μB/atom)	0.29	0.28	0.11
$\mu_{Pt\text{-}int}/\mu_{Ni\text{-}int}$	0.90	0.34	0.19

The experimental measurements (XMCD) and *ab initio* TB-LMTO results of reference [4] are also reported for comparison reasons.

(≈0.32 (±0.10)) μB/atom compared to the bulk (0.61 μB/atom). The authors contrasted these results against those obtained with the TB-LMTO method; they obtained 0.11 and 0.57 μB/atom for the Pt- and Ni- interfaces, respectively. moments. In the present work, we report a moment 0.28 μB/atom for Pt and a moment 0.83 μB/atom for Ni, both at the interface; this trend is in better agreement with that deduced from the XMCD data. The results are summarized in Table 2. The main difference with the other theoretical results is that the profiles of Fig. 2(b and c) show, with respect to the bulk, an increase of about 33% for the Ni moment at the interface.

The last column of Table 1 compares the values for the work function W_F obtained using LAPW against the experimental results coming from the references. There is agreement between both results, observing only a 3% variation for system Ni_7Pt_0 and 0.9% for system Ni_0Pt_7.

3.2. Electronic properties

Fig. 3 exhibits the LDOS (up and down) curves for the d bands, which are used for the study of electronic properties.

Let us first comment the results corresponding to Ni and Pt electronic structure. In Fig. 3(a and d) we present the LDOS for the 3d band of Ni surface and for the 5d band of Pt surface, respectively. Both correspond to the local electronic structure for the different atoms of the slab. The unbalance between the spin-up and the spin-down states (Fig. 3a) is expected to be the reason behind the magnetism of Ni.

We can observe that the width of the Ni(1 1 1) d band is about 4.5 eV (−5 to −0.5 eV), differing from those presented in Fig. 3(b and c), where the presence of Pt widens the d band by 2.5 eV.

At the same time, we underline that the qualitative trends in (3b down) and (3c down) are similar: the formation of Pt–Ni bonds increases the LDOS around the Fermi level with respect to Ni pure (3a down), showing a coupling between 3d Ni and 5d Pt electrons that induces a larger magnetic moment per Pt atom. For these systems, the hybridization effects and overlapping have a range within −3 and −0.5 eV. The relative importance of both, the structural and the chemical effects, through the interactions between the two components should be recognized.

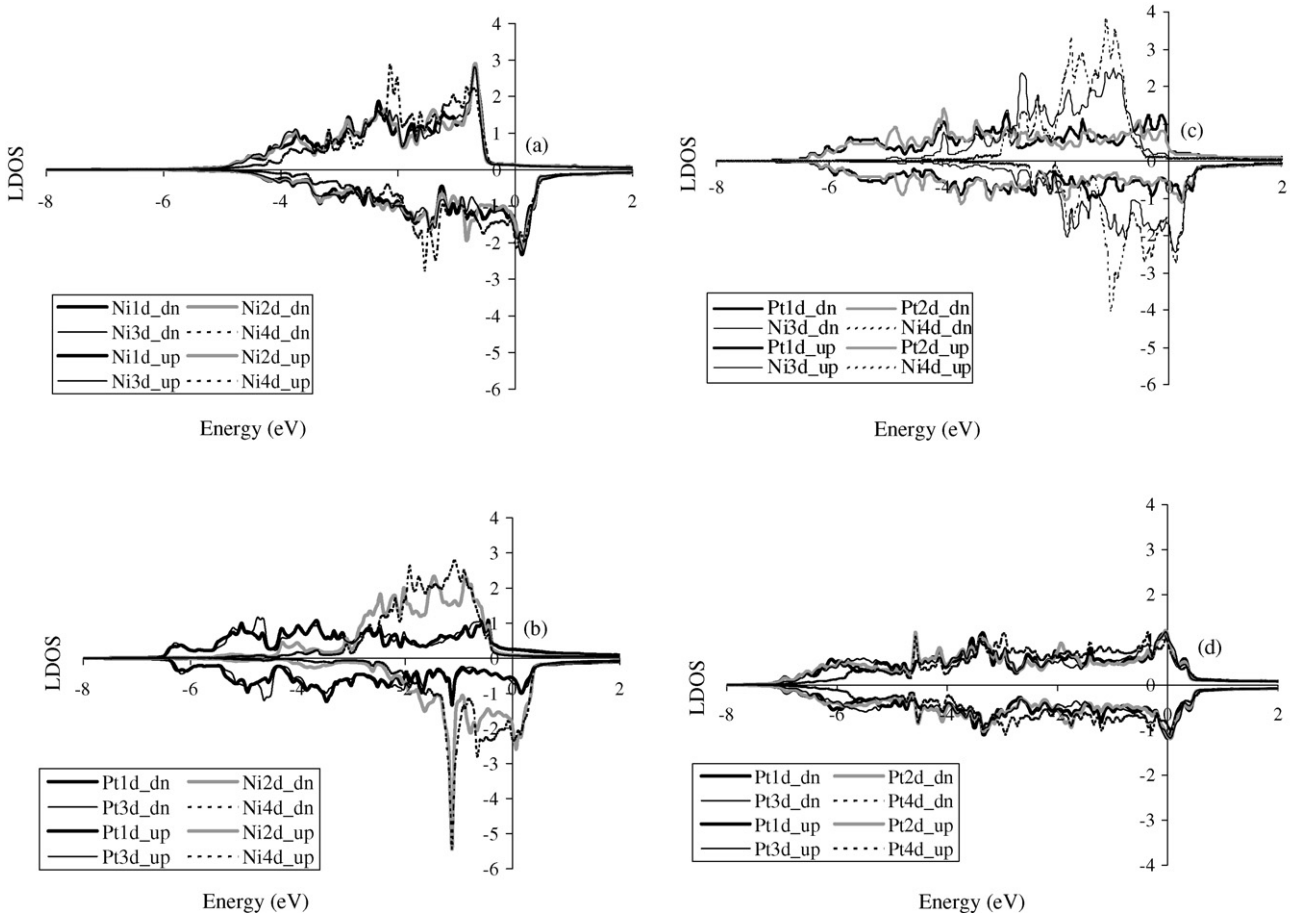

Fig. 3. Local density of states (LDOS) of the d-band obtained from a spin-polarized calculation for the systems Ni_7Pt_0 (a), $(Ni_1Pt_1)_3Ni_1$ (b), $Ni_2Pt_3Ni_2$ (c) and Ni_0Pt_7 (d). The origin of the energy scale corresponds to the Fermi level.

4. Conclusions

A GGA-DFT study of the magnetic and electronic properties of Ni_n/Pt_m(1 1 1) multilayer configurations, including Pt(1 1 1) and Ni(1 1 1) surfaces, was performed.

The optimised cell parameters for bulk Pt and bulk Ni were 3.98 and 3.53 Å, relaxing the experimental values by 1.5 and 0.3%, respectively. From these values the cell parameters for Pt(1 1 1), Ni(1 1 1) and bimetallic surfaces were obtained by means of a new optimisation.

The magnetism was studied by calculating the magnetic moments per atom for all these surfaces. We notice that the surface atom in the different bimetallic slabs has a magnetic moment which is enhanced from that of the respective center. On the interface, the non-ferromagnetic element acquires an induced μ improved by 50% with respect to that of surface Pt system (Pt_7) in a good concordance with previous experimental results and theoretical results. These effects may be attributed to hybridization at the interfaces.

The work function W_F values are in agreement with those obtained experimentally.

The electronic structure was analyzed using the concepts of the local density of orbital states. The LDOS curves for the d bands explain the phenomenon of magnetic induction in the multilayer configurations. The width of the Ni(1 1 1) d band is about 4.5 eV differing from those presented in the bimetallic systems, where the presence of Pt widens the d band by 2.5 eV.

The qualitative trends in the DOS down curves for $(Ni_1Pt_1)_3Ni_1$ and $Ni_2Pt_3Ni_2$ systems are similar: the formation of Pt–Ni bonds increases the LDOS around the Fermi level with respect to Ni pure, showing a coupling between 3*d* Ni and 5*d* Pt electrons that induces a larger magnetic moment per Pt atom. For these systems, the hybridization effects and overlapping have a range within -3 and -0.5 eV.

Acknowledgements

G.F.C. and N.J.C. are indebted to CONICET and Departamento de Física of UNS, Argentina, for financial support.

References

[1] J.W.H. duMond, J.P. Youtz, Phys. Rev. 48 (1935) 703.
[2] J.K. Schuller, Solid State Commun. 92 (1997) 141.
[3] I.K. Schuller, S. Kim, C. Leighton, J. Magn. Magn. Mater. 200 (1999) 571.
[4] F. Wilhelm, P. Poulopoulos, G. Ceballos, H. Wende, K. Baberschke, P. Srivastava, D. Benea, H. Ebert, M. Angelakeris, N.K. Flevaris, D. Niarchos, A. Rogalev, N.B. Brookes, Phys. Rev. Lett. 85 (2) (2000) 413.
[5] O. Robach, C. Quiros, H. Isern, P. Steadman, K.F. Peters, S. Ferrer, Phys. Rev. B 67 (2003) 220405.
[6] S.-C. Shin, G. Srinivas, Y.-S. Kim, M.-G. Kim, Appl. Phys. Lett. 73 (3) (1998) 393.
[7] G.F. Cabeza, N.J. Castellani, P. Légaré, J. Phys. Chem. 67 (2006) 690.
[8] J.P. Perdew, S. Burke, M. Ernzerhof, Phys. Rev. Let. 77 (1996) 3865.
[9] P. Blaha, K. Schwarz, G.A. Madsen, D. Kvasnicka and J. Luitz, WIEN2k (Karlheinz Schwrtz, Techn. Universit at Wien, Austria), ISBN 3-9501031-1-2 (2001).
[10] G.F. Cabeza, P. Légaré, N.J. Castellani, Surf. Sci. 457 (2000) 121.
[11] C. Kittel, Introduction to Solid State Physics, Wiley, New York, 1976p.465.
[12] S.Y. Choi, Y.S. Kwon, S.C. Hong, J.I. Lee, R.Q. Wu, J. Magn. Magn. Mater. 226–230 (2001) 1662.
[13] V.S. Fomenko, I.A. Podtshemaijeva, E.I. Adsorbtionnyje, Svojstva Materialov, Atomizadat, Moscow, 1975.
[14] D.R. Lide, CFC Handbook of Chemistry and Physics, 80th ed., CRC Press, New York, 1999.