J. Phys. D: Appl. Phys. 47 (2014) 105006 (11pp)

# Effects of surface charge doping on magnetic anisotropy in capping 3d–5d(4d) multilayers deposited on highly polarizable substrates

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Received 30 October 2013, revised 14 January 2014 Accepted for publication 15 January 2014 Published 19 February 2014

#### Abstract

We present a systematic study regarding the influence of surface charge doping on the magnetic anisotropy (MA) of capping 3d–5d/(4d) multilayers deposited on highly polarizable substrates such as Pt or Pd. The effects on the MA are investigated within a first-principles approach with a focus on Fe–Pt and Fe–Pd multilayers. For both layered systems, it is found that the MA is strongly altered upon charge doping, exhibiting different behaviour, however. A remarkable enhancement on the MA along with magnetization reversal is observed in Fe–Pt multilayers. In contrast, Fe–Pd multilayers have small MA energies as a consequence of their reduced orbital moments. Some MA features observed in the multilayers can be related with variations in the spin and orbital moment of the magnetic layers. Insights of the origin of the MA behaviour are investigated from a local perspective by analysing the d-orbital resolved local density of states in the framework of the second-order perturbation theory. Finally, the relation between the MA and orbital moments is discussed in terms of Bruno's formula.

Keywords: magnetic anisotropy, charge doping, multilayers

(Some figures may appear in colour only in the online journal)

#### 1. Introduction

Over the past years, diverse routes have been intensively explored for the manipulation and control of the electronic and magnetic properties on materials at an atomic scale with the aim of designing novel generations of electronic storage devices, mainly driven by their miniaturization [1–3]. Among the wide range of different manners for altering the local properties of the nanosized systems, applied magnetic fields [4], spin torque [5] and scanning tunnelling microscopy/atomic force microscopy (STM/AFM) magnetic tips [6] can be mentioned as the most common employed techniques. Nevertheless, very often these methods are nonlocal and experimentally very complex. External electric fields (EEFs), having the advantage of being localized, thereby emerge as a promising alternative in manipulating the magnetism of the systems [7]. Brovko and co-workers

performed an exhaustive review about the different ways of controlling the magnetism in metallic surfaces, pointing out the advantages of the electric fields over the magnetic ones and how the local magnetic properties with non-magnetic means can be tailored [8]. For instance, it has been shown that EEFs applied on ultra-thin films or aggregates and atomic chains deposited onto substrates can substantially modify magnetic properties such as exchange interactions [9] and more interestingly magnetic anisotropy (MA) energy [10, 11].

Another promising route to modify the magnetoelectric interactions of low-dimensional systems, used recently in materials science and nanotechnology, is through the change in the carrier density of the materials or charge doping. Surprisingly, direct charging has been found to display stronger effects on the magnetism than EEFs [12, 13]. In thin films, the excess of charge creates an effective charge trap increasing the Coulomb repulsion between the electrons in the surface,

the magnetic properties of such layered systems are thus drastically modified. Electrolyte charging [12, 14, 15] is a way to induce excess of charge in a material. Nevertheless, liquid electrolytes are needed to charge the systems. Novel and more effective local charge doping methods involve the usage of atomic tips [16–18]. Remarkably, not only the electronic and magnetic but the mechanical [19] and transport [20] properties of the systems are also extremely sensitive to the excess of charge. For instance, moderate charge doping of electrons (holes) on graphene can significantly enhance its ideal strength [19]. Similarly, through a change in the charge density carriers, the conductance of  $C_{60}$  fullerene deposited on Cu(1 1 1) considerably increases [20].

The MA of the nanoscale systems, being one of the fundamental parameters in novel electronic devices for data storage and processing, is particularly sensitive to the geometrical and chemical environment of the magnetic materials [21]. In thin films, the MA strength and direction of magnetization usually exhibit composition and thickness dependence [22]. Further, alloying 3d with 5d elements often leads to an enhancement of the MA [23]. Large MA values are essential to stabilize the orientation of magnetization in a material, nonetheless the low-energy spin-reorientation processes, crucial for reducing the size of the magnetic storage bits, become elusive. Thus, controlling the magnetic properties of the metallic multilayers, one of the cornerstones of the atomic-scale electronic devices, is important for building materials with specific properties.

In this context, Fe-Pt and Fe-Pd based multilayers are very attractive. Generally they display large magnetocrystalline anisotropy constants due to the large spin-orbitcoupling of the 5d electrons [24]. In disordered  $L1_0$  type systems, the FePt alloys are predicted to have the largest MA in comparison with other 3d-5d compounds such as FeNi, CoPt and CoPd [25] thereby becoming of particular interest for highdensity magneto-optical recording media [14, 26] Further, experiments [27] along with theoretical studies have shown that MA is more sensitive to the chemical order parameter than distortions. A change of 2 meV in the MA in FePt systems is predicted when increasing the order parameter [25]. First-principles calculations on Pt-Fe ultra-thin films report anisotropy energy values as large as 5 meV/magnetic atom [13, 28]. Moreover, it has been shown that the direction of magnetization can also be tailored. The Fe-Pt multilayer configuration is essential to attain perpendicular-oriented MA in FePt ordered alloy thin films [29]. In Fe-CoPd based multilayers the out-of plane MA strongly depends on the Fe-layer and can be tunable by varying the Fe thickness [30]. The search for alternative mechanisms that enable tuning the MA and direction of magnetization at an atomic scale is still in progress.

We extend our previous work [13] and show that surface charging is a promising mechanism for tailoring the MA of materials. The effects of the excess of charge on the MA in Fe–Pt and Fe–Pd based layers deposited on highly polarizable substrates such as Pt and Pd are systematically investigated. MA behaviour was found to be manifold. The MA of the multilayers is drastically altered upon charge doping. Remarkably, large MA enhancement and magnetization reversal, capping composition dependent, are observed.

The remainder of the paper is organized as follows: in section 2, the model and the employed theoretical methods are recalled. The effects of the charge doping on the structural stability, the role of capping, chemical composition and magnetic layers of the multilayers on the MA are investigated in sections 3, 4 and 5 respectively. The local magnetic properties are shown in section 6. In section 7 and 8 a simple model based on second-order perturbation theory along with Bruno's formula are presented for understanding the MA behaviour from a local perspective. Finally, in section 9, conclusions are provided.

#### 2. Theoretical methods

#### 2.1. Model

In the framework of the supercell approach, Fe–Pt(Pd) multilayers, arrangements of several atomic layers of Fe or Pt(Pd) deposited on highly polarizable substrates such as Pt or Pt, are modelled by means of a slab having 12–14 layers with ten of them representing the host Pt(Pd)-substrate. The large number of layers ensures that the occurrence of possible surface states in the substrate can be taken into account. Alternative approaches for electronic structure calculations such as the full potential (FP) [31], tight-binding (TB) [25] and exact (E) [32] linear muffin–tin orbital methods (LMTOs) in the level of the coherent potential approximation (CPA) are also suitable for investigating the electronic, magnetic and mechanical properties in multi-component alloys, finding in general, a good agreement with the supercell approach [32].

The surface charge doping is simulated through a uniform charge background in the supercell. In practice, this can be achieved by varying the number of valence electrons of the multilayers. It is found that by adding  $\sim$ 1 electron (hole) in the supercell is enough for simulating a realistic negative (positive) charge doping. An sketch of the model is presented in figure 1. The excess of charge mainly lies in both surfaces of the slab creating an effective charge trap. Consequently, due to the Coulomb repulsion between such excess of charge, very small charge (holes) oscillations inside the slab are generated. Nevertheless, as the thickness of the slab is increased the Coulomb repulsion reduces and the excess of charge lies only in the surface.

In order to qualitatively estimate the amount of charge diffused inside of the slab, we plot the charge distribution for electron (hole) doping taking  $Pt/Fe_2/Pt(100)$  as a example. The contour plot is shown in figure 2. Clearly, the excess of electrons mostly prevails in the surfaces of the slab with some noticeable diffusion in the first two atomic layers. As expected, the electron concentration near the surfaces reduces upon hole injection. From that result, one may infer that the electronic and magnetic properties of the multilayers will depend on the charge concentration in the slabs.

Further, for charged systems such slabs and deposited molecules on surfaces treated in the supercell approach, additional corrections to the total energy need to be considered.

P Ruiz-Díaz and V S Stepanyuk



**Figure 1.** Sketch of the uniform-charged background model for the 3d–5d(4d)-based multilayers. The vacuum space is taken to be at least 16 Å.



**Figure 2.** Charge distribution differences  $\rho_{\text{charged}} - \rho_0$  in Pt/Fe<sub>2</sub>/Pt(100) for (*a*) electron injection, 1.2 *e* (*b*) hole doping, 1.2 *h*. The difference is referred to as the neutral system,  $\rho_0$ .

These corrections arise as a direct consequence of the repetition of the supercell, thus the excess of charge needs to be compensated by a constant background jellium to keep the neutrality condition inside the supercell, otherwise the Coulomb energy would diverge [33]. The corrections (Makov–Payne corrections) are based on a multipole expansion and have the form [34]

$$E^{\infty} = E(L) + \frac{1}{\epsilon} \frac{\alpha q^2}{2L} + \frac{1}{\epsilon} \frac{2\pi q Q}{3L^3} + O(L^{-5}).$$
(1)

Here, q is the charge of the system,  $\alpha$  is the Madelung constant, L the supercell length and Q is the quadrupole moment caused by the excess of charge q [33, 34]. The leading term in this multipole expansion is the quadrupolar term. Since the excess of charge is not localized, the dipolar moment can be assumed to be zero. Nevertheless, the quadrupolar corrections [34] are not essential for determining the MA either. Following the expression (2.1), the corrected energy has the form  $E(\vec{m}, q, Q) = E(\vec{m}, q) + \Delta E_{corr}(q, Q)$ . In the first approximation, Q is scalar, namely  $\Delta E_{corr}(q, Q)$ is independent of the magnetization direction, hence the MA is independent of the quadrupolar corrections, i.e.  $MA = E(m_{\perp}, q, Q) - E(m_{\parallel}, q, Q)$  [13].

#### 2.2. Theoretical details

The ab initio calculations of the present work were carried out in the level of density functional theory (DFT) [35] following the implementation of the Vienna Ab initio Simulation Package (VASP) [36, 37]. The exchange and correlation interactions are treated by means of the Ceperley–Alder functional [38] in the local spin density approximation [39]. The magnetic anisotropy energy (MAE) of the multilayers is obtained in two steps: scalar-relativistic calculations are done for structural optimization, then the *spin-orbit* interaction is included for determining the MAE. A plane-wave basis set is employed with an energy cut-off of 400 eV. A k-grid of  $21 \times 21 \times 1$  is used in the scalar calculations and a denser one  $(29 \times 29 \times 1)$  when the spin-orbit interaction (relativistic calculations) is taken into account. Geometry optimization is reached when the forces on the atoms are less than  $10^{-2} \text{ eV } \text{\AA}^{-1}$  and the energy change between two successive electronic steps is less than  $10^{-7}$  eV. Such a strict criterion is essential for obtaining reliable MAEs

which are of the order of a few meV. In-plane and out-ofplane self-consistent calculations are performed for obtaining the MAE, i.e. E[001] - E[100]. Additionally, the magnetic force theorem was used [40], finding the same trends in the MA behaviour. In order to investigate the role of alloying on the MA we have considered Fe–Pt and Fe–Pd multilayers as representative examples of 3d/4d(5d) layered systems by taking into account several capping compositions.

#### 3. Charge-doping effects on the structural relaxation

In our study, the MAE of the multilayers essentially relies on two circumstances: the excess of charge strength and the capping composition. Yet, the charge doping may induce some structural deformations in the slabs due to the Coulomb repulsion, thereby affecting the MA value. Hence, it is worthwhile to first investigate the effects of the charge doping on the structural stability of the multilayers. In general, it was found that for both Fe-Pt(Pd) systems, the excess of the electrons (holes) leads to a small interlayer expansion (no more than 2%) in the two outermost layers yielding a nonappreciable change in the MA energy. As a particular example, we can mention the case of Pt/Fe/Pt(100), which exhibits a large MA. For hole doping (positive charging) we estimate an expansion between 0.2% and 1.2% for 0.6 and 1 hole per unit cell respectively. Similarly, for negative charging, a nonsignificant interlayer expansion is observed, indeed, in this case we found that the expansion is rather small, 0.1% and 0.35% for 0.6 and 1 e per unit cell respectively. Based on these results, one concludes that the charge doping modifies the structural stability of the slabs slightly, thus relaxation effects are not significant in the magnitude of the MA. Moreover, we have calculated MA explicitly as a function of the charge-doping strength for the unrelaxed and relaxed mentioned system finding variations in the MA of less than 1%.

### 4. Role of capping and chemical composition on the MA in metallic multilayers

#### 4.1. Fe-Pt multilayers

In order to investigate the effects of the surface charge doping on metallic thin films, the Fe-Pt multilayers are considered since they are widely known for displaying large MAs. The MA as a function of the charge (hole) doping for different capping compositions (one and two Fe-layers) is calculated. The results are summarized in figure 3. We start our study by calculating the MA of an Fe monolayer deposited on a Pt substrate as a function of the electron (hole) injection. First, as can be seen in figure 3(a), a strong dependence of the MA as a function of the excess of charge exhibiting nonmonotonic behaviour is found. At zero charge, MA reaches its minimum value (~0.25 meV/magnetic atom having an outof-plane axis of magnetization). For electron doping, MA rises up to 0.6 meV/magnetic atom for values around 0.6 e per unit cell and further increasing ( $\sim 25\%$ ) for larger electron concentrations. On the other hand, in the hole injection regime, MA enhances significantly up to 1.2 meV at 0.5 holes P Ruiz-Díaz and V S Stepanyuk decreasing to one half of this value ( $\sim 0.55 \text{ meV}$ ) at  $n \ge 0.9$ 

holes. The observed MA behaviour is the result of the interplay between the excess of charge and the existing strong spinorbit interaction at the interface. Finding a simple explanation for this trend is not straightforward. Moreover, it should be mentioned that by comparing the self and non-self calculations (magnetic force theorem), however the obtained MA values slightly differ from each other exhibiting similar tendencies. Further insights about the effects of the charge doping on the MA can be inferred from other capping compositions. For instance, by capping the former system with a Pt-layer, i.e. Pt/Fe/Pt(100), a completely different magnetic behaviour is obtained. In an earlier theoretical work, it has been shown that this particular layered system shows a relative large MA (5.12 meV/Fe atom) having an out-of-plane axis of magnetization [28]. Moreover, when an EEF is applied an enhancement of the order of  $\sim 13\%$  in MA is achieved. In agreement with these studies, we obtained an MA value of 5.4 meV/magnetic atom for a neutral system and out-ofplane axis of magnetization (figure 3(b)) [13]. Nonetheless, the EEF significantly alters the magnetic properties of the multilayers, the charge doping was found to have stronger effects on the MA than an EEF. The MA follows a linear trend with respect to the charge doping strength. Such behaviour has been also observed in the presence of EEF, although never achieving large values as in the presence of excess of charge. Its origin is often attributed to redistribution of the electrons near the Fermi level induced by the EEF [14, 28]. A remarkable MA enhancement of nearly  $\sim 65\%$  (8 meV/magnetic atom) around 1.2 holes/unit cell while a considerable reduction for electron doping of  $\sim 40\%$  (3 meV/magnetic atom at 1.2 e) with respect to the neutral system is determined. These variations represent a net change of  $\sim 95\%$  which is of the order of the MA for the neutral system itself [13]. The linearlike MA behaviour is not unique in the Fe-Pt multilayers but prevails for other capping compositions. It is also observed in Pt/Fe/Pt/Fe/Pt(100), Pt<sub>2</sub>/Fe/Pt(100) and partially in Fe/Pt/Fe/Pt(100), (figures 3(d), (e) and (c)) respectively. Nevertheless, it should be pointed out that in all these cases, the reached MA values for these particular capping compositions are smaller than in Pt/Fe/Pt(100).

Other Fe–Pt capping arrangements are also studied but they are presented in the next section in the context of the role of the magnetic layers in the MA.

#### 4.2. Fe-Pd multilayers

So far, it has been shown that the MA behaviour is capping dependent but also can rely on the chemical composition of the layers. To quantify how much it influences the MA, we review the Fe–Pd multilayers, which are one of the most typical 3d–4d alloys and are promising candidates for displaying large MAs. The MA for different capping compositions as a function of the charge doping strength is presented in figure 4.

Similarly as in the Fe–Pt multilayers, we first investigate how the MA in a single Fe monolayer deposited on a Pdsubstrate varies as a function of excess (lack) of charge. In this case, the MA is found not to be as sensitive to the



**Figure 3.** Calculated self-consistent (SC) and non-self-consistent (NSC) (magnetic force theorem) MAE (in meV/magnetic atom) for Fe–Pt multilayers having different capping compositions as a function of the injected charge (holes). The charge-doping scale (in units of *e*/unit cell) is referred to as the neutral system. Positive (negative) values stand for an excess (lack) of valence electrons. Positive (negative) MA values stand for an out (in-plane) axis of magnetization.

excess of charge as it was observed in the Fe-Pt interface (see figure 4(a)). In the non-charged system, the MA reaches 0.25 meV/Fe atom showing small variations, roughly  $\sim 5\%$ with respect to the neutral system for almost all the injected excess of charge. Only in the hole-doping regime (1.2  $\leq$  $n \leq 0.9$  h) the MA diminishes to 0.1 meV showing a small reorientation in the easy axis at once. Stronger effects in the MA are found in Pd/Fe/Pt(100). As can be seen in figure 4(b), a linear-like behaviour with opposite tendency regarding the Fe-Pt system counterpart is observed. Further, the MA values reached are somewhat smaller. They vary between 0.2 and 0.8 meV/Fe atom thereby favouring magnetization reversal, which occurs around  $\sim 0.2 e$ . Other Fe–Pd capping arrangements involving two alternating Fe-layers are also analysed (Fe/Pd/Fe/Pd(100) and Pd/Fe/Pd/Fe/Pd(100)) or two Pd-layers on top, Pd<sub>2</sub>/Fe/Pd(100), finding in all these cases a non-linear dependence on MA as a function of excess of charge strength (see figures 4(c), (d) and (e)). This behaviour may be attributed to a deeper influence of the charge doping due to the Coulomb repulsion in the electronic structure over the spin–orbit interaction of the Pd-layers, which seems to be not strong enough to stabilize the MA. Nevertheless, due to this relative small spin–orbit coupling (SOC) which is reflected in small MA values and orbital moments, a reorientation of the axis of magnetization is always observed in all the considered Fe–Pd multilayers. Fe–Pd multilayers having Fe-bilayers in their composition are analysed in the next section.

#### 5. Role of the magnetic layers in the MA

The magnetic behaviour of the Fe–Pt multilayers capped with iron bilayers is more striking. We have considered  $Pt/Fe_2/Pt(100)$ ,  $Pt_2/Fe_2/Pt(100)$  and  $Fe_2/Pt(100)$ . Unlike the Fe–Pt samples having single Fe-layers, the systems having



**Figure 4.** Calculated SC and NSC (force theorem) MAE (in meV/magnetic atom) for Fe–Pd multilayers having different capping compositions as a function of the injected charge (holes). The charge-doping scale (in units of *e*/unit cell) is referred to the neutral system. Positive (negative) values stand for an excess (lack) of valence electrons. Positive(negative) MA values stand for an out(in-plane) axis of magnetization.

Fe-bilayers display smaller MA values upon charge doping (see figures 3(f), (g) and (h)). In the case of the two first layered systems, they show an in-plane axis of magnetization at zero charge (~1.4 meV/magnetic atom and 0.5 meV/magnetic atom respectively). Due to their relative small MAs, these systems are potential candidates to exhibit magnetization reversal if the electronic environment is altered. Indeed, in all the samples mentioned above capped with Fe-bilayers, spin reorientation is observed upon hole injection. Furthermore, the linear relationship between MA and the charge doping vanishes showing a more complex dependence. When the multilayers are capped with one and two Pt-layers on top  $(Pt/Fe_2/Pt(100), Pt_2/Fe_2/Pt(100))$ , a similar MA behaviour is observed. For hole doping the MA increases to relative large values  $\sim 2.5$  meV/magnetic atom indicating the stability of the direction of magnetization. A reorientation in the axis of magnetization from in plane to out of plane is revealed and appears at 0.6 holes for both systems. The net changes

in the MA,  $\Delta$ MA =|MA(1.2)| – |MA(0)|, are estimated to be 1.3 meV/magnetic atom and 1.8 meV/magnetic atom with respect to the neutral value for Pt/Fe<sub>2</sub>/Pt(100) and Pt<sub>2</sub>/Fe<sub>2</sub>/Pt(100) respectively [13]. The variations found in the MA for the electron injection regime are less meaningful (~30–10%) remaining the easy-axis in plane. On the other hand, when the Fe-bilayer is capped on top, the MA exhibits a different behaviour regarding the former systems. The magnetization transition also occurs at 0.6 holes but MA has relatively smaller values ( $\leq 0.4$  meV) and decreases in the holedoping regime (figure 3(*f*)). From our analysis we conclude that the inclusion of the double Fe-layer in the multilayers is essential in the magnetization reversal.

In contrast, the inclusion of Fe-bilayers in the Fe–Pd systems does not significantly modify the MA behaviour as in the case of Fe–Pt multilayers. When a single iron bilayer caps the Pd-substrate (Fe<sub>2</sub>/Pd(100)), MA displays a non-monotonic dependence with respect to the charge doping



**Figure 5.** Spin of the magnetic (*a*), (*b*) and non-magnetic (*c*), (*d*) capping layers (in  $\mu_B$ ). (*e*) and (*f*) show the orbital difference in the Fe-layers ( $\Delta L = \mu_L^z - \mu_L^x$ ) between out and in-plane axis of magnetization (in  $10^{-2}\mu_B$ ). (*g*) A sketch of the X/Fe/X(100) multilayer system. For this case, the spin moment of the non-magnetic layer (X = Pt, Pd) is the average of the spin moment of both layers in direct contact with the magnetic layer (Fe).

strength, as can be seen in (figure 4(d)). However, if additional capping Pd-layers are added on top of the Fe-bilayers, for instance Pd/Fe<sub>2</sub>/Pd(100) and (Pd<sub>2</sub>/Fe<sub>2</sub>/Pd(100)), MA stabilizes showing a gradual enhancement from hole to electron injection (figures 4(g) and (*h*)). Moreover, the multilayers with Fe-bilayers display similar MA values that the ones having single or alternating Fe-layers (~0.2–0.3 meV/Fe atom). Nonetheless, for these layered systems, the Fe-bilayers are not essential in the magnetization reversal due to the relatively reduced MA values displayed in general.

## 6. Spin and orbital moments of Fe–Pt(Pd) multilayers

The variations of the spin moments show the influence of the charge doping on electronic and magnetic properties of the multilayers, but due to their robustness, it is not straightforward to follow a correspondence with subtle quantities such as the MA. Nevertheless, the orbital moment anisotropy (OMA, orbital moment differences between two magnetization directions) may reveal some MA features via the Bruno relation (MAE =  $-\frac{\xi_{Fe}}{4\mu_B}\Delta L_{Fe}$ ) [40]. This formula associates MA with the OMA of the magnetic films, particularly in 3d elements, and it will be reviewed in some detail in the next sections.

Hence, we calculate the spin and orbital moments of the Fe-layers and the neighbouring Pt(Pd)-layers as a function of the charge-doping strength. Spin and orbital moments are illustrated in figure 5. In the hole-doping regime, it is found that in both systems, the magnetic layers reach spin moments

close to the saturation value  $(3.2\mu_B \text{ assuming a bulk Fe d-band filling of 6.8 e)$  if the Fe-layer is on the surface. In the case of the capped iron bilayer, the magnetic moment slightly reduces as a result of an enhancement of the coordination number of the second Fe-layer. For other capping compositions (Pt or Pd the capping layer), a reduction of the spin moment of the order of ~15% for a fixed doping value is observed. When electrons are added to the multilayers, the spin moment further decreases since they occupy states above the Fermi level thus causing a reduction in the exchange splitting between majority and minority bands. The spin values reached in both layered systems are very similar, roughly 2.6–3.3 $\mu_B$ , which represents a net variation of ~20%.

Concerning the spin moment of non-magnetic layers at the interface, a high induced polarization is observed. The Pt(Pd)-layers in direct contact with the magnetic layers may exhibit spin moments up to  $0.45\mu_{\rm B}$  on average. Similarly to the Fe-layers, Pt and Pd develop the highest induced moment if they cap the multilayers e.g. Pt/Fe/Pt/Fe/Pt(100) and Pd/Fe/Pd/Fe/Pd(100), respectively. Other capping compositions display smaller magnetic moments, ~0.25–  $0.45\mu_{\rm B}$ , as can be appreciated in figure 5(*b*). A smooth and monotonous reduction of the magnetic moment is also observed upon charge doping.

We calculate the variations of the orbital moments between two axes of quantization; for simplicity, we take the out-ofplane and in-plane direction (z and x direction respectively). A strong dependence on the capping composition and chargedoping strength in both systems is found. The OMA does not follow a simple gradual depletion if the number of electrons is increased but a more complex non-linear behaviour (see figures 5(e) and (f)). OMA is minimum for systems featuring capping Fe-layers, particularly in Fe/X(100) and Fe/X/Fe/X(100) samples, being X = Pt, Pd. In contrast, OMA is maximum for systems having non-magnetic capping layers ( $X/Fe_2/X(100)$ ). Further, due to the stronger SOC of Pt, the Fe–Pt multilayers exhibit larger OMAs than Fe–Pd systems.

### 7. Electronic structure analysis: decomposed density of states

The origin of the MA behaviour found in the Fe–Pt(Pd) multilayers can be investigated from a local perspective by analysing the d-orbital-resolved local density of states (LDOS) of the magnetic layers through the second-order perturbation formula [41]:

$$\mathbf{MA} = E_x - E_z \sim \xi^2 \sum_{o,u} \frac{|\langle \psi_u | l_z | \psi_o \rangle|^2 - |\langle \psi_u | l_x | \psi_o \rangle|^2}{\epsilon_u - \epsilon_o}$$
(2)

where  $\{\psi_o, \psi_u\}$  stand for the unoccupied (occupied) states and  $\{l_x, l_z\}$  the angular momentum operators respectively. The  $\xi$  parameter is an average of the SOC coefficient.

The most important contributions to the MA come from the states near the Fermi level. Its behaviour is mainly governed by the denominator of equation (2). Furthermore, neglecting the spin flip terms between majority and minority states, the dominant changes in the MA can be only attributed to the coupling between states in the minority band. Hence, after analysing the SOC matrix elements between the different d-orbitals, MA trends can be qualitatively inferred. We choose some representative Fe-Pt(Pd) capping compositions. Pt/Fe/Pt/Fe/Pt(100) and Pt/Fe<sub>2</sub>/Pt(100) for Fe-Pt and Pd<sub>2</sub>/Fe<sub>2</sub>/Pd(100) and Pd/Fe/Pd(100) for Fe-Pd layered systems respectively. We start our discussion by analysing the Fe–Pt systems. In figure 6 the d-orbital resolved LDOS for the minority band is plotted, from where the MA trends can be traced since the majority band is fully occupied. In the case of systems featuring two Fe-layers in their composition, the d-LDOS refers to the average LDOS of the two magnetic Fe-layers. In the case of Pt/Fe/Pt/Fe/Pt(100), we found that the MA trends presented in figure 3(d) are mainly governed by the coupling between the  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals, and the observed linear behaviour can be explained. First, such coupling favours an out-of-plane direction of magnetization. Secondly, the  $d_{xy}$  orbitals undergo a monotonic depletion near the Fermi level upon hole doping reducing the contribution of the fist term of equation (2) to MA. Thus, this reduction enhances MA in the hole-doping regime.

Despite not finding a clear dominant contribution of some particular coupling between the different d-orbitals in Pt/Fe<sub>2</sub>/Pt(100) as can be seen in figure 6(b), the main trends of the MA through the d-resolved LDOS analysis can be inferred anyway. The orbitals showing the stronger variations near the Fermi level are the d<sub>xy</sub> and d<sub>xz</sub> orbitals. The coupling between these orbitals through the l<sub>x</sub> operator reduces upon hole doping

enhancing MA. In contrast, in the electron injection regime, the couplings favouring the in-plane easy axis become dominant while the ones boosting the out-plane magnetization decrease, such as  $\langle d_{x^2-y^2} || d_{xy} \rangle$ , thereby leading to an in-plane axis of magnetization.

A similar analysis is carried out for the Fe–Pd multilayers. Starting with Pd<sub>2</sub>/Fe<sub>2</sub>/Pd(1 0 0), we plot the d-resolved LDOS shown in figure 7(*a*). Here, the couplings  $\langle d_{xy} || d_{xz} \rangle$  and  $\langle d_{x^2-y^2} || d_{yz} \rangle$  give the main contribution to the MA. Both couplings rise upon hole doping favouring an in-plane axis of magnetization, while the later one reduces as the electrons are injected into the system leading to a smooth transition of the easy axis from in-to-out of plane axis of magnetization as can be appreciated in figure 4(*h*).

For Pd/Fe/Pd(100), only the couplings  $\langle d_{x^2-y^2} || d_{xy} \rangle$ and  $\langle d_{z^2} || d_{yz} \rangle$  play a role. Such couplings favour different directions of magnetization. The interplay between the couplings essentially yields a linear transition in the magnetization from in-to-out of plane at moderate excess of charge values (see figure 4(*b*)). In conclusion, we can see that the MA trends in metallic multilayers can be successfully explained, to a large extent, by the second-order perturbation theory. The most dominant couplings, favouring a particular direction of magnetization, determine the direction of the easy axis.

#### 8. Relationship between MA and orbital anisotropy

The simplest model that can explain the MA in magnetic ultrathin films is known as Bruno's relation, which relates the MA with the orbital moment variations, MAE =  $-\frac{\xi_{Fe}}{4\mu_{\rm p}}\Delta L_{\rm Fe}$  [40]. It assumes a direct correspondence between OMA and MA. Nevertheless, experimental results together with ab initio calculations calculations [42] show that Bruno's formula is a particular case valid for systems where only the on-site contributions to the MA are considered and the exchange splitting is substantial (strong magnets). Further, in the case of strong hybridizations the spin-flip contributions become important, such as in the case of large SOCs, then a simple correspondence between MA and OMA is not valid anymore. Andersson et al showed that in the case of alloyed compounds, the spin-dependent orbital contribution and the SOC of all the atomic species need to be taken into account in the form MAE =  $\sum_{q\sigma\sigma'} \Delta E_q^{\sigma\sigma'}$ , where  $\Delta E_q^{\sigma\sigma} = \sigma \frac{\xi_q}{4\mu_{\rm B}} \Delta L_q^{\sigma}$  with  $\sigma$  and q standing for the the spin and atomic species respectively [42]. Our results suggest that some multilayer systems follow Bruno's relation. This finding is remarkable since both formulas were derived for non-charged systems. Moreover, for 3d-4d [21] and 3d-5d [28] ultra-thin films has been shown that the main contribution to the total MAE comes from the non-magnetic layers<sup>1</sup>, hence a linear correspondence between MAE and OMA could not be simply inferred. Therefore, it

<sup>&</sup>lt;sup>1</sup> The non-magnetic layers (Pt and Pd) exhibit larger orbital moments than in the Fe-layers. In our approach, layer-resolved MAE analysis is not possible, thus a layer contribution to the MA cannot be quantified. However, the OMA for the non-magnetic layers (Pt and Pt) in direct contact with the magnetic ones displays the same trends as the OMA of the Fe-layers discussed in the present work



Figure 6. Decomposed minority d-orbital LDOS for the magnetic layers in Fe–Pt systems depicted in figure 3, for same representative charge-doping values.

is interesting to investigate under which conditions Bruno's formula could be employed.

In the case of Fe–Pt multilayers, we found that only Pt/Fe/Pt(100) and Pt/Fe/Pt/Fe/Pt(100) fulfil Bruno's formula, while other capping compositions partially do, such is the case of  $Pt/Fe_2/Pt(100)$  (see figure 8(a)). Thus, for these particular systems, the charge doping cannot substantially alter the hybridizations induced by the spin–orbit interaction between the Fe and Pt layers. Only in the later layered system is a slight deviation observed from the linear behaviour beyond a certain charge threshold, indicating that the hybridizations become important upon electron doping for this particular case. A non-linear dependence between OMA and MA in general is observed showing that the hybridizations along with the strong SOCs of the Pt-layers are strong enough and cannot be tuned by charge-doping injection. This is the typical scenario of the multilayers capped with Fe-bilayers.

For Fe–Pd multilayers, a direct correspondence between OMA and MA is less evident. A partial linear-like behaviour can be only appreciated in Pd/Fe/Pd(100) and  $Pd/Fe_2/Pd(100)$  multilayers. In general, a disperse

distribution of MA as a function of OMA is obtained (see figure 8(b)). The relatively small SOC of the Pd-layers does not enable the multilayers to develop large orbital moments and consequently reduced MAs are obtained.

From our analysis we can conclude that a direct relationship between OMA and MA (quantified by Bruno's formula) can be found in systems featuring moderate hybridizations between magnetic and non-magnetic layers, such in the case of some Fe–Pt capping compositions. It has been demonstrated that these interactions can be tuned through charge injection and the linear correspondence is not preserved beyond a certain charge threshold (mostly in the electron-doping regime). Moreover, a non-gradual behaviour upon charge injection in the MA is followed in systems having small SOCs, such as in the case of the Fe–Pd multilayers, leading in most cases to a non-direct correspondence between the MA and OMA.

Hence, the interplay between the SOC and d–d hybridizations rule the magnitude of MA and the direction of magnetization at once.



Figure 7. Decomposed minority d-orbital LDOS for the magnetic layers in Fe–Pd systems depicted in figure 4, for same representative charge-doping values.



**Figure 8.** Relationship between magnetic anisotropy (MAE) per magnetic layer and OMA ( $\Delta L = \mu_L^z - \mu_L^x$ ) for (*a*) Fe–Pt, (*b*) Fe–Pd multilayers as a function of electron (hole) doping.

#### 9. Conclusion

As a general remark, we have systematically investigated the surface charging effects on MA in capping 3d/4d-5d multilayers deposited on highly polarized substrates. Surface charging results in direct consequences in both magnitude and direction of magnetization. The substrate via the spin-orbit coupling and hybridizations with the magnetic layers is found to play a major role in the magnetic properties of the multilayers upon charge doping. The large spin-orbit coupling of the non-magnetic layers determine the MA magnitude and the hybridizations can be tuned by the excess of charge (holes). Significant enhancement in the MA is obtained in Fe-Pt multilayers and explained qualitatively in terms of the secondorder perturbation theory. Further, in capped multilayers featuring Fe-bilayers, a spin reorientation occurs due to an enhancement of the hybridization caused by both alloying and charge doping. The Fe-Pd multilayers display reduced MAs, thus easy axis switching is always observed upon charge doping independently of the capping composition. Some MA features observed in the multilayers can be traced to the spin and orbital moment variations of the magnetic layers.

As a conclusion, it is shown that the charge doping alters the magnetic properties of metallic thin films strongly. Thus, it can be employed as a promising technique for controlling the electronic and magnetic properties of novel materials.

#### Acknowledgments

We thank O O Brovko and T R Dasa for stimulating discussions in the improvement of the present manuscript. This work was supported by the Deutsche Forschungsgemeinschaft (DFF) through SFB 762 and the DFG project 'Structure and magnetism of cluster ensembles on metal surfaces: microscopic theory of the fundamental interactions'.

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