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Band-filling effects in the magnetic anisotropy of atomic thin layers of Co

S. Gallego[a]*, M.C. Muñoz[a], L. Szunyogh[b] and P. Weinberger[c]

[a]*Instituto de Ciencia de Materiales de Madrid, CSIC, 28049 Cantoblanco, Madrid, Spain;* [b]*Department of Theoretical Physics, Budapest University of Technology and Economics, Budafoki u. 8., H-1111 Budapest, Hungary;* [c]*Center for Computational Nanoscience, Seilerstätte 10/22, A-1010 Vienna, Austria*

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Ultrathin Co layers grown on Ru(0001) form a unique structure, which shows a variety of spin reorientation transitions linked to the completion of atomic layers. The close relation between atomic layer completion and magnetic anisotropy is maintained when Co is covered by thin noble metal films. Here we explore the effect of different metal cappings with unfilled *d* shell based on fully relativistic calculations within the Screened Korringa-Kohn-Rostoker (SKKR) method. The complex interplay of electronic and surface contributions is determined by means of a layer-resolved analysis, which allows us to predict the conditions leading to perpendicular magnetization for ultrathin Co films.

Keywords: magnetic anisotropy; Co; ultrathin films; capping layers

1. Introduction

The study of thin films with high perpendicular magnetic anisotropy (PMA) has been one of the most active research topics during the past few years, with relevant technological implications in the development of magnetic memory devices [1]. The breaking symmetry of a surface/interface introduces an enhancement of the magnetic anisotropy energy (MAE) from the μeV scale typical of bulk systems to the meV. On the other hand, there are many factors competing subtlety in the determination of the final MAE of any system [2,3]: the magnetic dipole-dipole interaction, which dominates thick films, favours an in-plane orientation of the magnetic easy axis, while the magnetoelastic and magneto-crystalline anisotropies strongly depend on the atomic characteristics of the system: chemical order, lattice parameter, strain, etc. [2–6]. Thus, to determine which are the conditions to obtain PMA, detailed theoretical calculations are required.

Within an *ab-initio* approach, the uniaxial MAE of a surface or thin film is obtained from the difference between the total energies of the system with the magnetization normal

*Corresponding author. Email: sgallego@icmm.csic.es

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to the surface, and contained in the surface plane. The individual total energies are about seven orders of magnitude larger than their difference, which imposes severe precision requirements on the computation of the MAE [7,8]. For this reason, early calculations based on the perturbative inclusion of the spin-orbit interaction led to poor evaluation of the MA. The development and implementation of fully-relativistic *ab-initio* methods has thus been one of the major achievements in the field [7,8].

An interesting phenomenon related to the MA is the existence of spin-reorientation transitions (SRTs) in ultrathin magnetic films [3]: in systems with PMA, increasing the film thickness changes the orientation of the magnetization to the in-plane direction, due to the dominance of the magnetic dipole–dipole term. These SRTs can also be induced by external agents, like thermal effects, coatings or magnetic fields [9,10,11]. More unusual is the existence of inverse SRTs, when the magnetization reverses from in-plane to perpendicular as the film thickness is enlarged [9,10]. For systems showing an inverse SRT, a second SRT takes place for thick enough films, as the magnetostatic term dominates. Less common is the existence of a multiple SRT for ultrathin films below 10 ML. In particular, only two systems are known to exhibit this property, namely Fe/W(110) and Co/Ru(0001) [14,15,16]. For the second one, a close relation exists between the completion of atomic layers and the SRT, which helps us to understand the microscopic mechanisms behind the SRT. The strain in the Co film, the existence of stacking faults and the electronic effects at the interface with the adjacent media are the key ingredients governing the final magnetic anisotropy (MA).

A rich behaviour can be obtained when, in addition, the ultrathin magnetic films are covered by non-magnetic cap metals [17,18]. The cap influences in several ways: on one hand, the structure of the covering layers affects that of the underlying film, imposing additional strain conditions in the presence of lattice mismatch. On the other hand, the electronic interactions at the interface with the cap modify the magnetocrystalline contributions, especially when the cap introduces a strong spin-orbit coupling (SOC), as occurs for Au or Pt. The resulting MA is also effected by the cap film thickness, so that a large number of parameters are involved in the final value of the MA.

In a previous study we determined the influence of noble metal capping in the SRT of ultrathin Co films under 10 atomic layers [19]. Here we explore the effect of different metal caps with incomplete *d* shell, focusing on a metal with less valence electrons than Co (Ru) and others with a more filled *d* shell and a high SOC (Pt). This paper is organized as follows: first, the computational framework and the conditions of the calculations are introduced. Then, we present the electronic and magnetic properties of Co films of different thicknesses covered with cap films of Ru or Pt, also analyzing the influence of the cap thickness. Finally, we focus on the MA, separating the study of cap films one monolayer (ML) thick from thicker coverages, and comparing with the results previously obtained for noble metal capping.

2. Computational details

Our calculations are based on the relativistic, spin-polarized Screened Korringa-Kohn-Rostoker (SKKR) method for layered systems [20]. For each structure considered, the effective potentials and effective exchange fields are obtained self-consistently using 180 $\mathbf{k}_{\parallel}$ points in the irreducible wedge of the surface Brillouin zone. Energy integrations are

performed along a semicircular contour using a 16-point Gaussian sampling on an asymmetric mesh. The maximum orbital quantum number is set to 2. Dipole terms are included in the Madelung constants.

The magnetic anisotropy energy (MAE) is determined based on the magnetic force theorem [21,22]. For a given structure, the MAE is defined as

$$\begin{aligned} \mathrm{MAE} &= \Delta E_{\mathrm{b}} + \Delta E_{\mathrm{dd}} \\ \Delta E_{\mathrm{b}} &= E_{\mathrm{b}}(\|) - E_{\mathrm{b}}(\perp) \\ \Delta E_{\mathrm{dd}} &= E_{\mathrm{dd}}(\|) - E_{\mathrm{dd}}(\perp), \end{aligned}$$

where ΔE_{b} and ΔE_{dd} are the band energy and classical magnetic dipole–dipole energy contributions, respectively. The symbols $\perp$ and $\|$ refer to the magnetic configurations with the magnetization perpendicular to the surface and parallel to it, respectively. In this way, a positive MAE corresponds to a preferential axis of the magnetization pointing along the normal surface. The value of ΔE_{dd} is calculated in a classical framework, solving the magnetostatic Poisson equation [23]. ΔE_{b} is obtained by the SKKR method, using an energy-dependent k-sampling, which includes up to $3.9 \cdot 10^4$ $\mathbf{k}_{\|}$ points to achieve convergence. The structures we have modelled are thin Co films 2–10 ML thick on a Ru(0001) substrate, either bare or covered by a metal capping of 1–10 ML thickness. The results presented here correspond to covering layers formed by Pt or Ru, although they will be compared with previous calculations of noble metal cap films [19]. Within the SKKR we are forced to use a common two-dimensional (2D) lattice parameter ($a_{2\mathrm{D}}$) for all layers of a given structure. Bulk Co presents an hcp structure of $a_{2\mathrm{D}} = 2.51$ Å at the (0001) planes, while for hcp Ru(0001) $a_{2\mathrm{D}} = 2.71$ Å. Pt is an fcc metal of $a_{2\mathrm{D}} = 2.77$ Å at the hexagonal (111) planes. In a previous work [19] we showed that the 2D strain induced in the Co film has a determinant effect in the MAE, so that expanded $a_{2\mathrm{D}}$ values favour PMA. Co on Ru(0001) starts growing epitaxially for 1 ML thick films, and then initiates a gradual 2D contraction toward the hcp Co lattice [16,24]. Noble cap metals also tend to maintain their own lattice parameter, even for a large lattice mismatch between Co and cap [19]. In order to compare the different cap/Co/Ru(0001) structures, we have chosen the intermediate $a_{2\mathrm{D}}$ value corresponding to the Ru(0001) lattice, although we will consider the effect of different values on the main results. In addition, to recover the atomic volume corresponding to each element, interlayer relaxations (Δd) are introduced. The results presented here correspond to Δd values of -6% for the Co layers, and $+6\%$ for Pt, both with respect to the Ru interlayer distance. At the metal/Co interfaces, the nonuniform relaxation introduced in [16] is used.

3. Interface effects

We will start analyzing the changes induced by a cap layer on the electronic properties and magnetic moments of the Co film. Bare Co films exhibit a significant spillover of the electronic charge towards the vacuum at the outermost surface layer. The presence of the surface also narrows the energy distribution of electronic states, leading to an enhancement of the magnetic moments. For example, for a 10 ML thick film, the value of the spin (m_S) and orbital (m_L) components of the magnetic moment are, respectively, 1.70 and $0.12\,\mu_B$ at an inner layer and 1.79 and $0.13\,\mu_B$ at the surface plane. Although the existence of m_L is important regarding the MA, for the particular properties evaluated in

this section it is enough to consider m_S, as the orbital components are effected by the well-known quenching, typical of transition metals.

When Co is covered by a 1 ML cap, the charge and moment distributions close to the surface are significantly altered. In Figure 1 we show the layer-resolved values of the charge and spin moments corresponding to a 4 ML thick Co film covered by 1 ML Pt or Ru, also including the values for noble metal caps (Cu, Ag and Au). The charge values (ΔQ) are obtained as the difference between the bulk metal charge and the actual

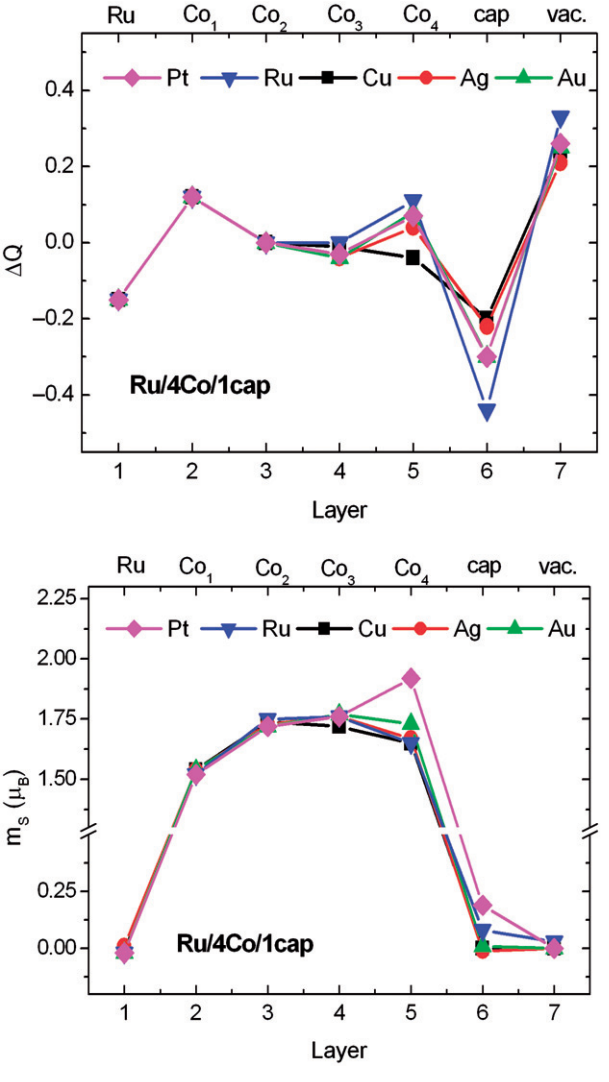

Figure 1. Layer resolved (top) valence charge (referred to the bulk metal value) and (bottom) spin magnetic moment of a 4 ML thick Co film on Ru(0001) covered by 1 ML of either Cu (black squares), Ag (red circles), Au (green up triangles), Ru (blue down triangles) or Pt (pink diamonds). Layers are numbered from the substrate Ru plane at the interface with Co (layer 1) to the surface; the first vacuum layer (layer 7) is included to show the charge spillover.

charge in the system. Notice that the ΔQ of Au and Pt are almost identical. It is evident from the figure that for all cases, significant charge rearrangements occur at both Co interfaces (with the substrate and with the cap) always leading to a charge gain for Co. The presence of the surface also has an important influence on the cap charge distribution, inducing a spillover towards the vacuum. The charge transfer from the cap to Co is larger the less filled the *d* shell is, thus noble metal caps show the lesser transfer, while Ru provides the largest one, both as a cap and as a substrate layer. On the other hand, the interface effects are very localized, involving only the two or three layers close to the interface.

This range of interface effects is similar for the magnetic moments, and again the spin-polarization induced by Co is more significant for Ru and Pt than for the noble metals. In particular, the almost closed *d* shell of Pt makes it a highly polarizable material, and in fact the largest m_S are obtained at the interface with Pt, both for Co and for the cap atoms. On the other hand, the fast damping of the interface effects makes these values almost independent of the Co thickness for Co films >2 ML. This is evidenced in Figure 2 for the cap m_S: although the moment induced at each metal is different, for a fixed cap element there are few variations depending on the Co thickness. As a result, the largest net magnetization corresponds to the Pt capped films, ranging from $3.6\,\mu_B$ for 2 ML Co to $10.4\,\mu_B$ for the thickest 6 ML Co films.

The situation for thicker capping can be regarded in Figure 3. The outermost surface layer suffers a significant charge spillover toward the vacuum, while there is a charge redistribution at the Co/cap interface. As the charge spillover induced by the surface has been displaced from the Co/cap interface, the interface charge transfer is comparable to that at the Co/substrate interface. Although the differences between cap elements are minor, the largest charge transfer takes place from Ru to Co. Concerning the magnetic moments, the induced spin polarization mainly affects the cap plane in contact with Co, and the largest m_S values clearly correspond to Pt, which in addition is the only cap element favouring a ferromagnetic alignment between Co and cap. Compared to

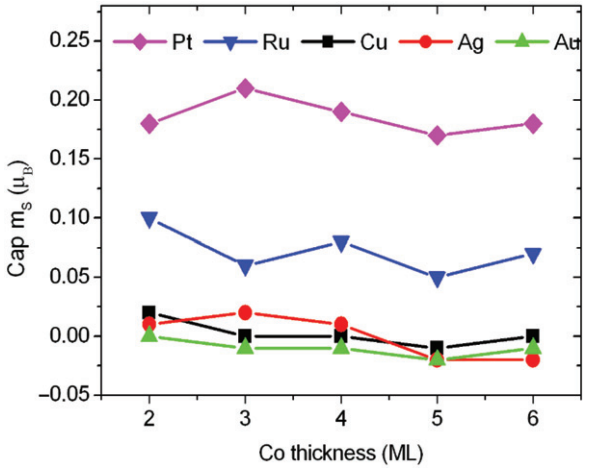

Figure 2. Spin magnetic moment of the cap layer as a function of the Co film thickness for Co films covered with 1 ML of either Pt, Ru, Cu, Ag or Au.

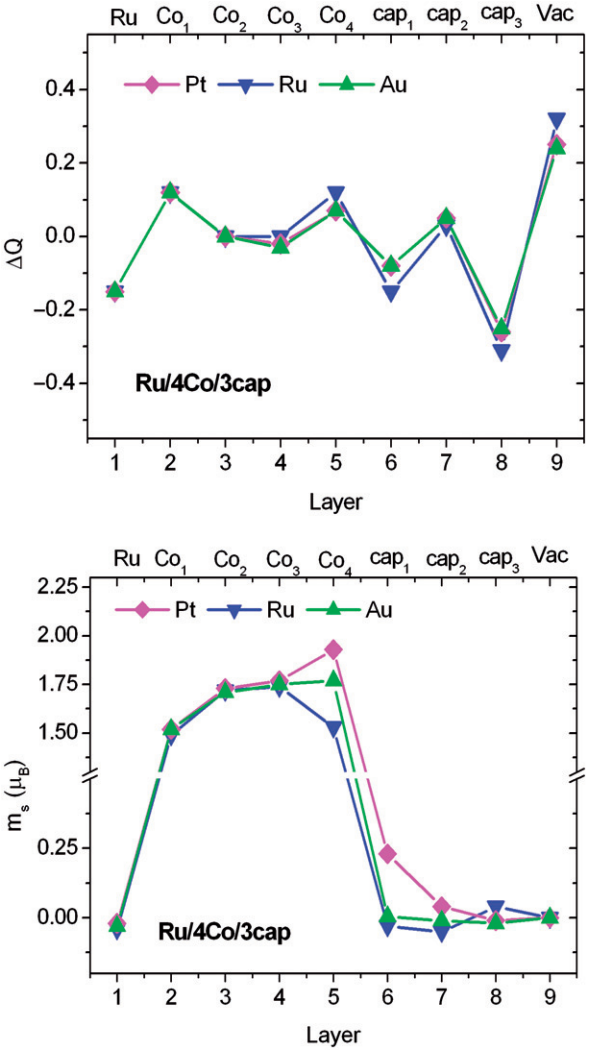

Figure 3. Same as Figure 1 for 3 ML thick cap films.

the noble metals, Ru and Pt induce the largest variations in the Co m_S, although in opposite directions: while the presence of Pt enhances the Co magnetization, Ru lowers it. To summarize, the highest magnetization among all ultrathin Co films studied here, corresponds to the Pt capped films, and in particular, to the 6 ML thick Co films capped by 2 ML Pt with a net magnetization of 10.6 μ_B.

4. Magnetic anisotropy

As mentioned in the introduction, the PMA of a thin film is determined by a delicate balance of terms, which in turn depend on a complicated interplay of structural and electronic parameters. In our previous study of Co/Ru(0001) covered by noble metals, we

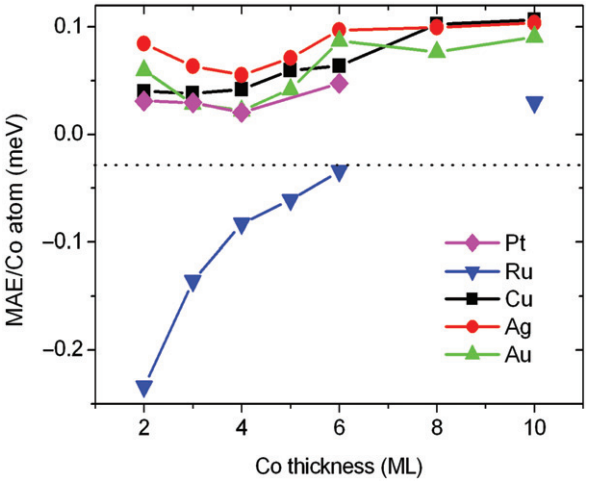

Figure 4. Total MAE normalized to the number of Co atoms for Co films of different thicknesses capped by 1 ML metal film.

identified which conditions favour PMA in ultrathin Co films: an expanded a_{2D} with respect to the bulk hcp Co lattice, the ultrathin thickness and an enhancement of the SOC, which may be introduced by the presence of a cap layer [19]. As both Ru and Pt have a larger a_{2D} than Co, they may favour the onset of the first condition; in addition, Pt shows a high SOC. The results presented here have been obtained using the a_{2D} of Ru, which is intermediate between Co and Pt. This is representative of the effects at the interface layers and at thin Co films, although for thicker Co films a reduction of the layer-resolved contributions to the MAE is expected due to the reduction of a_{2D} towards the Co lattice. This would lead to negative MAE (in-plane easy-axis of magnetization) for the thicker Co films.

4.1. *Capping with 1 ML thick films*

First, we will present our results for Co films of different thickness covered by 1 ML Pt or Ru. The value of the MAE is represented in Figure 4 for Co films of 2–10 ML thickness, normalized to the number of Co layers to ease comparison between the different structures. For the thinnest films, the MAE is dominated by the interface effects, and large differences in the MA occur depending on the chemical nature of the cap. As the Co thickness is increased, the contribution from the inner layers dominates the interface, and a tendency to a common value of the MAE can be observed for all systems. Although the absence of SRT is due to the expanded lattice used in these calculations, the interface effects are captured: while Ru tends to reduce the MAE, Pt behaves similarly to the noble metal caps, allowing the achievement of high PMA.

A more detailed analysis can be performed in the light of the layer-resolved band-energy contributions of Figure 5. The largest ΔE_b always corresponds to the subsurface Co plane. In the case of Pt, there is a significant enhancement of this maximum ΔE_b with respect to the bare film, and the high value remains almost independent of the

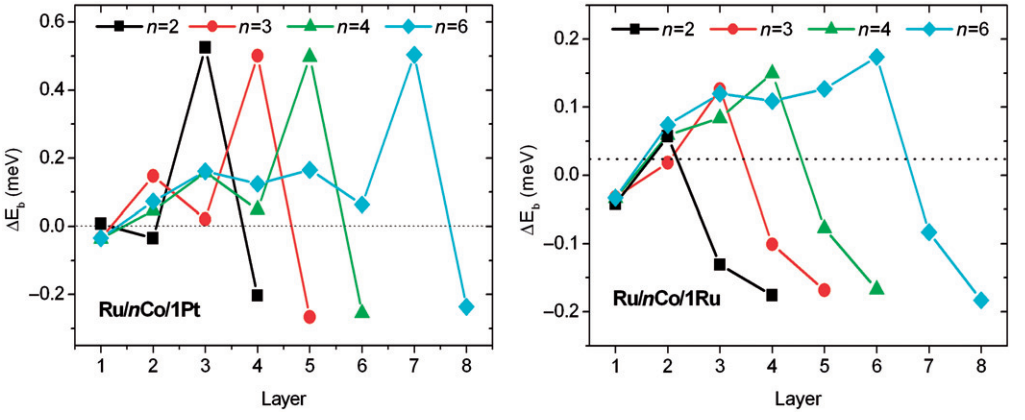

Figure 5. Layer-resolved band energy contribution of Co films of different thicknesses (n) capped by 1 ML Pt (left) or Ru (right). Layer numbering follows the convention of Figure 1, the first point of each curve referring to the outermost substrate Ru plane (layer 1) and the last one to the cap layer at the surface.

Co film thickness. The moderate difference between the MAE corresponding to a Pt or a noble metal cap comes from the ΔE_b at the cap layer, which is large and negative for Pt and negligible for noble metals.

A different situation arises from Ru, which always lowers the enhancement of the interface Co ΔE_b term. The effect is so strong that it dominates the inner layers' contribution up to thicknesses of ~8 ML (see Figure 4). On the other hand, and similarly to Pt, the interface effect is not very dependent on the Co film thickness: the apparent increase of ΔE_b for thicker Co films actually comes from the higher background imposed by the inner layers when they adopt an expanded hcp structure. This independence of ΔE_b on the Co thickness, even for the ultrathin Co films, is at odds with the results obtained for noble metal caps.

4.2. *Thick cap films*

As the cap thickness is increased, the interface becomes buried by a non-magnetic metal, and thus one would expect a reduction of the MAE. This is what happens for noble metal caps except in the case of high SOC (i.e. Au), where an enhancement of the interface ΔE_b occurs leading to a large PMA, even for thick cap films. In Figure 6 we compare the MAE of Co films of different thicknesses when bare or covered by 1–3 ML of Ru or Pt. The layer-resolved ΔE_b contributions for the 2 and 3 ML thick cap films is shown in Figure 7. Depending on the nature of the cap element, the results are very different. Similarly to the case of Au, a 2 ML thick Pt cap induces a considerable increase of MAE, while for 3 ML Pt the MAE is reduced, even leading to a SRT to in-plane magnetization. The ΔE_b shows the origin of this result: while Pt does not reduce the interface Co ΔE_b, as expected from its high SOC, it acquires a high negative ΔE_b on its own, which effectively reduces the global MAE. This effect is more significant the larger the number of contributing Pt layers.

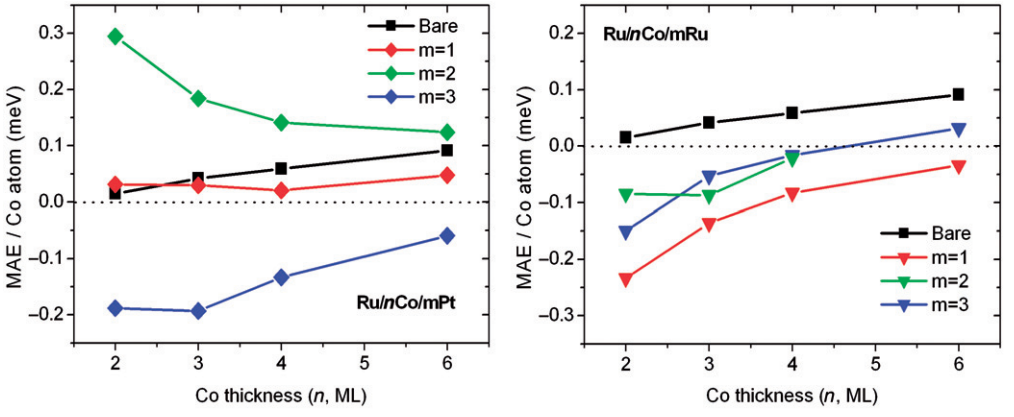

Figure 6. Same as Figure 4 for (left) Pt and (right) Ru cap films of different thicknesses.

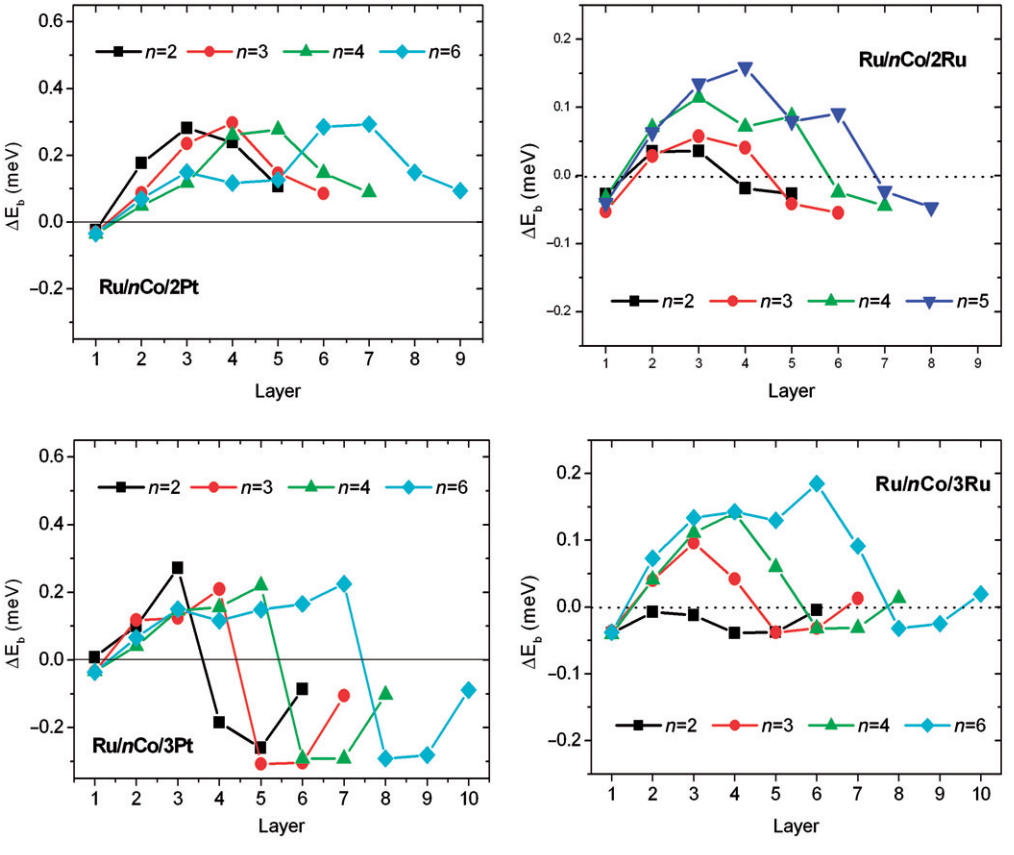

Figure 7. Same as Figure 5 for cap films of (top) 2 ML and (bottom) 3 ML thickness.

A different situation arises for Ru, which strongly favours an in-plane magnetization. We will concentrate on the thinnest Co films, where the interface contribution is more relevant. The presence of a Ru cap always provides an in-plane magnetization, no matter what the cap thickness. However, as the cap film thickens from 1 ML and the Co/cap interface is buried, there is an effective increase of the MAE. This is partially due to the damping of the surface effects, which reduces the absolute value of the (negative) MAE. But in addition, there is a real enhancement of the layer-resolved ΔE_b contributions: first, the negative subsurface Co term changes to a positive value for 2 and 3 ML thick Ru caps; in addition, the Ru ΔE_b becomes extremely enhanced, and it even becomes positive for certain configurations (surface term for 3 ML thick cap).

5. Conclusions

By means of fully relativistic calculations of ultrathin Co/Ru(0001) films capped by Ru and Pt, we have shown the importance of band-filling effects in the final MAE of the system. The evolution of the MAE upon the cap film thickness depends, in a significant way, on the electronic structure of the cap film. In general, Ru tends to lower the MA, favouring an in-plane magnetization. For Pt, large PMA can be obtained for a wide range of Co thicknesses when the number of Pt layers is below three. Due to the important SOC of Pt, the high MAE is comparable to that obtained with Au capping. Moreover, the large spin-polarizability of Pt favours an increase in the net magnetization of the system.

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