Magnetic anisotropy of transition-metal interfaces analyzed from a local perspective

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Layer-resolved electronic self-consistent calculations of magnetic anisotropy energies (MAE's) are reported that explain the capping-induced transition to perpendicular magnetization observed in Co films on Pd(111). The interfaces responsible for the stability of the off-plane easy axis are characterized microscopically. A local analysis of the MAE's as a function of Co thickness reveals an unexpected internal magnetic structure of the Co-Pd interfaces in which the magnetic moments and spin-orbit interactions at Pd atoms play a crucial role. Trends for different $3d$ and $4d$ overlayers are discussed.

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In past years, magnetic nanostructures involving transition metals (TM's) have been the focus of an intense and sustained research activity which is driven to a large extent by the quest for new materials with specific applications.[1] Ultrathin films with stable perpendicular magnetization, one of the major early discoveries in this field,[2–5] remain a subject of central interest from both fundamental and technological standpoints.[6–8] A particularly relevant example of tailoring magnetic behavior at a nanoscopic scale is the experimental observation that magnetization reorientation transitions can be induced by modifying the interfaces of magnetic materials, for example, by capping thin magnetic films with non-magnetic elements.[3–5] Measurements on Co films deposited on Pd(111) show that the easy axis of uncovered $\mathrm{Co}_m/\mathrm{Pd}(111)$ is within the film plane, even for the monolayer ($m = 1$), while capped $\mathrm{Pd}_n/\mathrm{Co}_m/\mathrm{Pd}(111)$ present an off-plane easy axis already for $n \geq 1$ ($m \leq 8$).[5] A similar stabilization of perpendicular magnetization in thin Co films has been observed after Cr capping.[6] The control and understanding of these phenomena at an atomic level constitutes a central issue in current research on magnetism with considerable implications for the development of magnetic nanostructures at surfaces.

The reorientation transitions are often interpreted phenomenologically in terms of bulk, interface, and surface contributions to the magnetic anisotropy energy (MAE).[1,5,6] The idea of associating a specific MAE to each interface, which goes back to Néel,[9] is both physically appealing and of proven efficacy. Still, from a fundamental point of view, the challenge remains to characterize the dominant interfaces and to identify the microscopic mechanisms underlying such a remarkable environment dependence of the MAE. The purpose of this letter is to present a comprehensive theoretical description of the magnetic anisotropy at the interfaces of capped magnetic thin films as a function of film thickness, taking $\mathrm{Pd}_n/\mathrm{Co}_m/\mathrm{Pd}(111)$ as a particularly relevant example. An analysis of our results from a local perspective allows to identify the atomic layers corresponding to each interface, the various local contributions to the interface MAE (IMAE), and the interactions favoring perpendicular magnetization. In this way a consistent understanding of the whole set of systematic experimental observations on $\mathrm{Pd}_n/\mathrm{Co}_m/\mathrm{Pd}(111)$ is achieved for the first time.[5]

Several situations leading to perpendicular magnetization in ultrathin films have already been investigated theoretically.[8] The stability of the off-plane magnetization direction has been traced back to modifications of the electronic structure and spin-orbit (SO) energies due to reduced dimensionality, quantum confinement, changes in film structure, and substrate-hybridization effects. However, none of these mechanisms seems to apply properly to Co-films on Pd since in this case, the redistributions of the spin-polarized density at the interfaces, and in particular the magnetic moments induced at the Pd atoms, are expected to play a major role. Taking into account that the SO interactions are very sensitive to the details of the electronic spectrum, we perform accurate self-consistent calculations for each orientation of the magnetization $\vec{M}$ and derive the MAE in a non-perturbative way as difference between electronic energies. We consider a self-consistent tight-binding Hamiltonian given by the sum of three terms: the inter-atomic hopping term H_0, the Coulomb interaction term H_C, and the SO coupling term H_{SO}.[11] For each magnetization direction δ the local densities of electronic states (DOS) $\rho^{\delta}_{l\alpha\sigma}(\varepsilon)$ at layer l, orbital α, and spin σ are determined self-consistently by treating H_0, H_C and H_{SO} on the same footing. The δ-dependent energy is then calculated as $E_\delta = E^{\mathrm{DD}}_\delta + E^{\mathrm{MC}}_\delta$. E^{DD}_δ refers to the dipol-interaction term and $E^{\mathrm{MC}}_\delta = \sum_l E^{\mathrm{MC}}_\delta(l)$ stands for the electronic or magneto-crystalline (MC) energy which can be written as the sum of layer-resolved contributions

$$E^{MC}_\delta(l) = \sum_{\alpha\sigma} \Big[\int_{-\infty}^{\varepsilon_F} \varepsilon\, \rho^{\delta}_{l\alpha\sigma}(\varepsilon)\, d\varepsilon \; - E^{\mathrm{dc}}_{l\alpha\sigma} \Big] \,. \qquad (1)$$

Here $E^{\mathrm{dc}}_{l\alpha\sigma}$ corrects for the double counting of Coulomb interactions. Finally, the MAE is given by $\Delta E = E_x - E_z$ where $\delta = z$, is the direction perpendicular to the film, along (111), and $\delta = x$, the in-plane direction parallel to a nearest-neighbor bond, along $(1\bar{1}0)$.

The parameters used for the calculations are specified as follows. The two center hopping integrals are given by the canonical expression in terms of the corresponding bulk band widths[11]. The intra-atomic d-electron exchange integrals J yield the proper magnetic moment and exchange splitting in the solid ($J_{\rm Co} = 0.76$ eV). For non-magnetic elements J is obtained from local spin-density calculations ($J_{\rm Pd} = 0.52$ eV).[12] The values of the SO-coupling constant ξ are taken from Ref.[10] ($\xi_{\rm Co} = 88$ meV and $\xi_{\rm Pd} = 200$ meV). Concerning the film structure we assume for simplicity a perfect (111) layer-by-layer epitaxial growth with the interlayer distances taken from bulk Co for Co-Co, from bulk Pd for Pd-Pd, and the average of them for Co-Pd.[13] In practice, the local DOS and the spin-polarized charge densities are calculated self-consistently in all Co or capping layers and including up to 4–6 layers of the Pd substrate. In fact, one observes that beyond the 4th layer the spin-density distribution of the substrate is practically the same as in bulk Pd.

Fig. 1 summarizes our results for the MAE of thin $\rm Pd_n/Co_m/Pd(111)$ films for $1 \le m \le 8$ and $n = 0, 1$. For the uncapped films ($n = 0$) the easy axis is within the film plane already for the monolayer. As m increases, dipol-dipol (DD) interactions tend to stabilize the in-plane direction further yielding a monotonic decrease of the $\Delta E = E_x - E_z$. Pd-capped Co thin films show a qualitatively different behavior. For a single layer of Pd capping ($n = 1$) the Co monolayer ($m = 1$) presents an off-plane magnetization with a rather large $\Delta E = 0.4$ meV. This can be phenomenologically attributed to the changes in the film interfaces, namely, to the replacement of a Co surface by a Co-Pd interface. As the Co-film thickness m increases, ΔE decreases mainly due to the growing importance of the DD contribution $\Delta E^{DD} < 0$. Therefore, for thick enough films ΔE^{DD} dominates over ΔE^{MC} and $\vec{M}$ turns back to the in-plane. The transition from off-plane to in-plane magnetization is obtained for $m = 7$–8. Notice that all these calculated reorientation transitions, before and after capping and as a function of m, are in good agreement with torsion-oscillation magnetometry experiments.[5] In the following the microscopic origin of this remarkable behavior is investigated.

The stability of perpendicular magnetization originates in the electronic contributions E_δ^{MC} to the MAE, particularly in the orientation dependence of spin-orbit interactions. Therefore, the following analysis shall be focused on the magneto-crystalline anisotropy energy ΔE^{MC}. Taking advantage of our local approach one may express $\Delta E^{MC} = \sum_l \Delta E^{MC}(l)$ as a sum of layer-resolved contributions

$$\Delta E^{MC}(l) = E_x^{MC}(l) - E_z^{MC}(l) \ , \qquad (2)$$

where $E_\delta^{MC}(l)$ are given by Eq. (1). Thus, the magneto-anisotropic properties can be related to the various local atomic environments. First of all, let us consider the uncapped films. Results for $\Delta E^{MC}(l)$ in $\rm Co_m/Pd(111)$ are given in Fig. 2 as a function of m. The surface Co-layer ($l = 1$) gives the most important local contribution $\Delta E^{MC}(1)$ which depends rather weakly on m. $\Delta E^{MC}(1)$ favors an in-plane orientation of $\vec{M}$, the actual easy axis for uncapped films. In contrast, at the Co-Pd substrate interface the local anisotropy energies $\Delta E^{MC}(l)$ of each layer are very sensitive to m showing strong oscillations and even changes of sign. For example, the Pd (Co) contribution tends to stabilize the in-plane (off-plane) direction for for $m = 2$ while for $m \ge 3$ the opposite trend holds. No simple physical picture can be extracted by considering the single-layer contributions separately. The situation changes completely if one regards the interface instead of the layers as the relevant physical entity. Fig. 2 shows results for the Co-Pd interface anisotropy energy $\Delta E_I(\rm Co/Pd)$ as given by the sum of $\Delta E^{MC}(l)$ for the two adjacent Co and Pd layers. One observes that $\Delta E_I = \Delta E^{MC}_{\rm Co}(m) + \Delta E^{MC}_{\rm Pd}(m+1)$ depends weakly on m favoring clearly a perpendicular orientation of $\vec{M}$ [$\Delta E_I(\rm Co/Pd) > 0$ for all m]. The observed in-plane easy axis of uncovered films can now be understood as the superposition of surface and interface anisotropies, the former being the dominant one. In fact, if one would neglect the surface-layer contribution $\Delta E^{MC}(1)$ the magnetization of ultrathin Co films would be off-plane since $\Delta E_I(\rm Co/Pd) \simeq 0.3$ meV is larger than the ΔE_{DD} for $m \le 3$. Already at this stage one may infer that if the Co-surface, for which $\Delta E^{MC}(1) < 0$, would be replaced by a Co-Pd interface having $\Delta E_I(\rm Co/Pd) > 0$, an off-plane magnetization of the film should be induced.

Results for $\Delta E^{MC}(l)$ and ΔE_I at the substrate interface of $\rm Pd_1/Co_m/Pd(111)$ films are given in Fig. 3(a). Comparison with Fig. 2 shows that the single-layer contributions are very sensitive to the presence of a capping layer. In particular the trends in the even-odd oscillations of $\Delta E^{MC}(l)$ for small m are reversed, as if a capped m-layer Co-film would behave somewhat like an uncapped film with $m + 1$ layers. However, it is remarkable that despite such a strong m dependence of $\Delta E^{MC}(l)$, the Co-Pd substrate interface MAE remains approximately independent of m, and is not much affected quantitatively by the presence of capping, even for the smallest m ($\Delta E_I \simeq 0.25$–0.30 meV).

The local MAE's at the capping Co-Pd interface, shown in Fig. 3(b), reveal additional interesting features. In this case the oscillations of $\Delta E^{MC}(l)$ are much stronger than at the substrate and the convergence to the thick-film limit is slower. Still, the interface MAE $\Delta E_I = \Delta E^{MC}_{\rm Co}(1) + \Delta E^{MC}_{\rm Pd}(0)$ preserves its identity and depends weakly on m. Notice that now both interfaces favor a perpendicular magnetization ($\Delta E_I > 0$). The reorientation transition can then be understood microscopically as the result of replacing a negative Co-surface anisotropy energy, which favors in-plane magnetization, by a positive Co-Pd interface anisotropy energy which favors off-plane orientation. For single-layer Pd capping ($n = 1$) ΔE_I is significantly larger at the overlayer interface ($\Delta E_I \simeq 0.5$ meV) than at the substrate interface ($\Delta E_I \simeq 0.3$meV).

The difference in ΔE_I can be related to an enhancement of the local magnetic moments $\mu_{\rm Pd}(0)$ at the Pd atoms of the capping monolayer as compared to the moments of the Pd substrate layers. In fact, for the overlayer we obtain $\mu_{\rm Pd}(0) = 0.45\mu_B$ while at the uppermost substrate layer $\mu_{\rm Pd}(m+1) = 0.30\mu_B$. The enhancement of $\mu_{\rm Pd}(0)$ is a consequence of the reduced local coordination number at the Pd capping monolayer and essentially disappears with increasing overlayer thickness n. Indeed, calculations for Pd$_2$/Co$_3$/Pd(111) and Pd$_2$/Co$_4$/Pd(111) yield $\mu_{\rm Pd}(0) = 0.35\mu_B$ and $\Delta E_I = 0.32$ meV at the capping interface, values which are both close to the substrate-interface results.

A closer look at the layer-resolved contributions to the interface MAE's in Figs. 3(a) and 3(b) shows that, in almost all cases, it is Pd and not Co, which gives the largest $\Delta E^{MC}(l)$, often defining the sign of ΔE_I. The Pd layers cannot be regarded as a mere means of modifying the Co-film electronic structure but rather as important magnetic components on their own. The Pd atoms carry non-vanishing induced magnetic moments at the interface and, as $4d$ elements, are subject to significant spin-orbit couplings ($\xi_{\rm Pd} \simeq 2\xi_{\rm Co}$).[10] It is therefore very reasonable that they contribute to ΔE_I and to the overall MAE of these films. In order to explore the matter further a few test calculations have been performed for different hypothetical situations. First, taking Pd/Co$_2$/Pd(111) and Pd/Co$_3$/Pd(111) as representative examples, we have determined the MAE by imposing vanishing local magnetic moments $\mu(l)$ at the Pd atoms and obtained $\Delta E_I < 0$. Remarkably, the same result follows when self-consistent non-vanishing μ(Pd) are allowed but only the Pd SO coupling $\xi_{\rm Pd}$ is switched off. The crucial role of Pd layers on the interface MAE and on the magnetization-reversal transition is thereby demonstrated. These results also confirm the importance of a self-consistent determination of spin-polarized density, electronic structure, and spin-orbit interactions.

Concerning the Co layers it is interesting to observe that the local orbital magnetic moments $L_\delta(l)$ ($\delta = x$ and z) are significantly enhanced, typically by a factor two, with respect the Co-bulk value $L_b = 0.13\mu_B$ [$L(l) = 0.20 - 0.24\mu_B$ for Co atoms]. The anisotropy of $L_\delta(l)$ follows the changes in easy axis of the film. For instance, at the surface of uncapped Co films, $L_x(1) > L_z(1)$ while at the interface of capped films $L_x(1) < L_z(1)$. Moreover, $L_x(1) > L_z(1)$ also if the inplane magnetization direction of capped films is artificially stabilized by setting $\xi_{\rm Pd} = 0$ or $\mu_{\rm Pd} = 0$. However, the magnetization direction δ giving the largest $L_\delta(l)$ does not always coincide with the direction with the lowest local energy $E_\delta^{MC}(l)$.

In order to investigate the specificity of Pd as capping element and the possible effect of changes in the *sp-d* charge transfers we have performed calculations of the MAE of a capped 3-layer Co film X$_1$/Co$_3$/Pd(111) as a function of the d-band filling n_d of the capping transition metal X. The d-electron exchange integral and hopping elements of Co (Pd) are used for the overlayer as representative values for $3d$ ($4d$) TM's. Our results show that the capping-interface ΔE_I oscillates as a function n_d being positive around $n_d = 5$, 7 and 9 and negative around $n_d = 6$ and 8. The quantitative values of ΔE_I and the precise ranges of n_d for positive and negative ΔE_I depend on whether $3d$ or $4d$ TM's are considered. This is mainly due to the different ratios J/W between the d-electron exchange integral and band width. Rather large negative ΔE_I are obtained for Co, Rh, and Nb. In contrast, Cr, Fe, and Pd capping favor off-plane magnetization. Finally, for Ni and Ru, ΔE_I is small and the tendency is less clear. In particular for values of n_d close to that of Pd ($9.0 \leq n_d \leq 9.5$) we find $0.10 \leq \Delta E_I \leq 0.65$ meV, which indicates a stable off-plane magnetization. Large $\Delta E_I \simeq 0.6$ meV are also obtained for Cr, in good agreement with the recent observation of perpendicular magnetization in Cr/Co$_m$/Pd(111) films.[6] Changing the capping material offers certainly interesting possibilities of tailoring the interface MAE. Whether off-plane anisotropy is favored or not, may depend subtly on material specific parameters such as band filling and Coulomb interaction strength, thus defying easy generalizations.

In conclusion, the magnetic anisotropy at the interfaces of Co-Pd thin films have been investigated. The MAE's have been determined self-consistently as a function of film thickness with and without capping overlayers. For the first time, the relevant interface MAE's responsible for the experimentally observed capping-induced reorientation transitions have been identified from a microscopic perspective. A detailed local analysis revealed, moreover, that the Co-Pd interfaces present a remarkable internal magnetic structure with Pd contributions playing a dominant role. Besides the interest of these specific systems, the present local approach should preserve its relevance as a means of understanding the magneto-anisotropic behavior at TM interfaces, which has significant implications for magnetism at the nanoscale.

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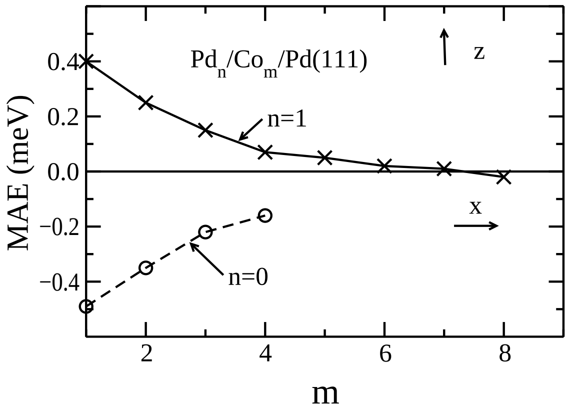

FIG. 1: Magnetic anisotropy energy $\Delta E = E_x - E_z$ of Pd$_n$/Co$_m$/Pd(111) as a function of Co-film thickness m, where x (z) refers to the in-plane (off-plane) magnetization direction.

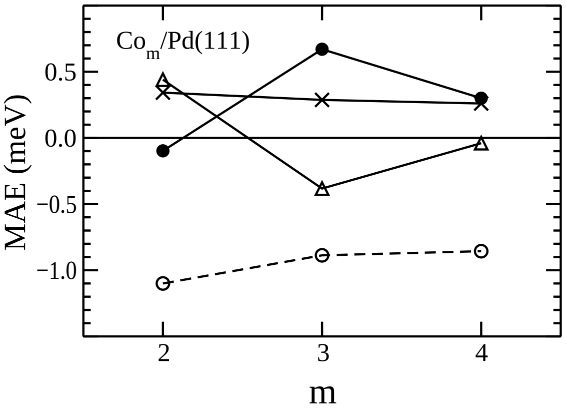

FIG. 2: Local magneto-crystalline anisotropy energy $\Delta E^{MC}(l) = E_x^{MC}(l) - E_z^{MC}(l)$ of uncapped Co$_m$/Pd(111) as a function of m. Results are given for the surface Co layer ($l = 1$, circles), for the interface Co layer ($l = m$, triangles), for the interface Pd layer ($l = m + 1$, dots), and for the Co-Pd interface anisotropy $\Delta E_I = \Delta E_{\mathrm{Co}}^{MC}(m) + \Delta E_{\mathrm{Pd}}^{MC}(m+1)$ (crosses).

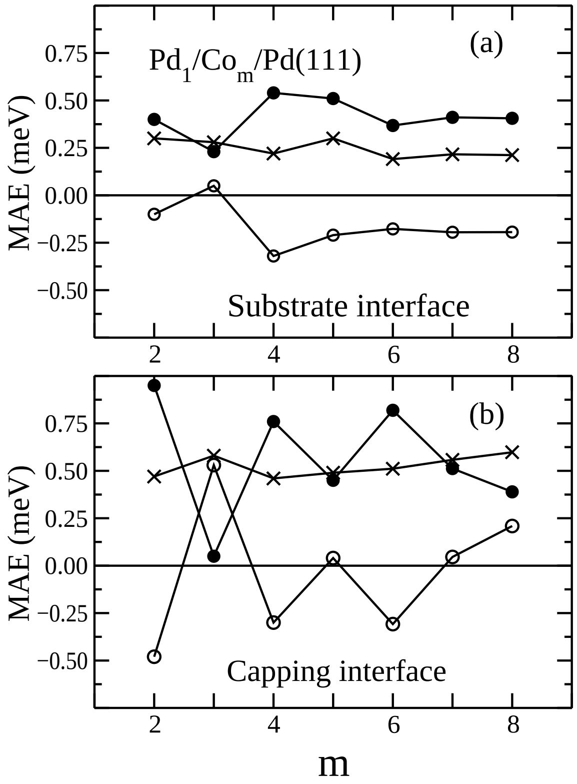

FIG. 3: Local magneto-crystalline anisotropy energy $\Delta E^{MC}(l) = E_x^{MC}(l) - E_z^{MC}(l)$ of capped $\mathrm{Pd}_1/\mathrm{Co}_m/\mathrm{Pd}(111)$ as a function of m. (a) Substrate interface: Co layer $l = m$ (circles), Pd layer $l = m + 1$ (dots), and Co-Pd interface anisotropy $\Delta E_I = \Delta E^{MC}_{\mathrm{Co}}(m) + \Delta E^{MC}_{\mathrm{Pd}}(m+1)$ (crosses). (b) Capping interface: capping Pd layer ($l = 0$, dots), subsurface Co layer ($l = 1$, circles), and Co-Pd interface anisotropy $\Delta E_I = \Delta E^{MC}_{\mathrm{Co}}(1) + \Delta E^{MC}_{\mathrm{Pd}}(0)$ (crosses).