

Magnetic properties of $(\text{Co}_n\text{Pd}_m)_r$ superstructures on Pd(100) and Pd(111)

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Abstract. The magnetic properties of $(\text{Co}_n\text{Pd}_m)_r$ superstructures on Pd(100) and Pd(111) are evaluated using the fully-relativistic spin-polarized screened Korringa-Kohn-Rostoker method. It is found that only in the case of a Pd(111) substrate such superstructures exhibit perpendicular magnetism, while on a Pd(100) substrate the magnetization is oriented in-plane. Also investigated is the effect of interdiffusion in repeated superstructures. By using the inhomogeneous coherent potential approximation (CPA) for layered systems the effect of ordering into (repeated) superstructures can be described in an *ab-initio*-like manner. It is found that already small amounts of interdiffusion can be decisive for the actual value of the magnetic anisotropy energy.

PACS. 75.70.Cn Interfacial magnetic properties (multilayers, magnetic quantum wells, superlattices, magnetic heterostructures) – 71. Electronic structure

1 Introduction

Co/Pd superstructures on suitable substrates raised considerable interest because of possible applications for magneto-optical storage media. In quite a few experimental papers [1–6] various aspects of perpendicular magnetism in these systems were discussed, in particular the exceptionally strong dependence on the (surface) orientation of the substrate. In the theoretical papers on this topic [7–11] not only magneto-optical properties of ordered and disordered bulk systems [7,8] were calculated using different theoretical and computational schemes, but also in a preliminary manner the question of the magnetic anisotropy and its microscopic sources was addressed.

The aim of this paper is to present a theoretical study of the magnetic properties of $(\text{Co}_n\text{Pd}_m)_r$ superstructures on Pd by varying the sequence of Co and Pd layers, *i.e.*, by varying n and m and the number of repetitions r , and to discuss the effect of the growth direction, *i.e.*, the effect of the surface orientation of Pd serving as substrate. In addition to the ordered superstructures, interdiffusion at the Co/Pd interfaces will be discussed for exactly that system which, when ordered completely, has the highest perpendicular magnetic anisotropy energy per repetition.

2 Computational aspects

All calculations were performed using the fully-relativistic spin-polarized screened Korringa-Kohn-Rostoker method [12–14]. In all cases the effective potentials and effective exchange fields were obtained self-consistently based on the exchange-correlation functional given in reference [15], by making use of surface Brillouin zone integrations with 45 k_{\parallel} vectors per irreducible wedge (ISBZ), and a “buffer” of three Pd layers to the semi-infinite Pd substrate. The band energy differences ΔE_b between a uniform perpendicular-to-plane and a uniform in-plane orientation of the magnetization was then evaluated in terms of the magnetic force theorem (see also Ref. [16]) using 990 k_{\parallel} vectors per ISBZ (for further computational details see Refs. [17–19]), guaranteeing well-converged quantities. For describing interdiffusion the CPA for layered systems [20] was applied using the same numerical parameters just mentioned.

All calculations refer to the experimental lattice spacing ($a_0 = 7.3530$ a.u.) of a Pd fcc “parent lattice” [21], *i.e.*, no layer relaxations were considered although in principle this would be possible [18]. It should be noted that in the case of a Pd(100) substrate the (constant) interlayer spacing (3.6765 a.u.) is substantially shorter than for a Pd(111) substrate (4.2454 a.u.).

As is well-known, the magnetic anisotropy energy ΔE_a consists of two contributions, the band energy term

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ΔE_b and the magnetic dipole-dipole contribution ΔE_{dd} , usually referred to as shape anisotropy. Suppose a multilayer system consists of N layers of a statistically disordered binary alloy of constituents A and B on top of some metallic substrate. If c_α^p denotes the respective concentrations of the constituents A and B in layer p then in terms of the (inhomogeneous) CPA for layered systems [20] ΔE_b is given by

$$\Delta E_b = \sum_{p=1}^N \sum_{\alpha=A,B} c_\alpha^p \Delta E_\alpha^p, \quad (1)$$

where the ΔE_α^p ,

$$\Delta E_\alpha^p = \int_{\epsilon_b}^{\epsilon_F} \Delta n_\alpha^p(\epsilon) (\epsilon - \epsilon_F) d\epsilon, \quad (2)$$

refer to component- and layer-resolved contributions to the band energy. In equation (2) $\Delta n_\alpha^p(\epsilon)$ is the difference of the component and layer projected DOS with respect to the given orientations of the magnetization, ϵ_b the bottom of the valence band and ϵ_F the Fermi energy of the nonmagnetic substrate. It should be noted that ΔE_b (1) replaces the total energy difference with respect to the prechosen orientations of the magnetization, since within the magnetic force theorem both the potentials as well as the exchange fields are considered to be unchanged.

Suppose now that in a system of the type $\text{Pd}(hkl)/(\text{Co}_n\text{Pd}_m)_r$ interdiffusion over two layers at the Co/Pd interfaces occurs. Starting at the substrate side for the first n layers the concentrations for Co and Pd are then given by

$$c_{\text{Co}}^p = \begin{cases} c \\ 1 \\ c \end{cases}, \quad c_{\text{Pd}}^p = \begin{cases} 1-c \\ 0 \\ 1-c \end{cases}, \quad p = \begin{cases} 1 \\ 2, \dots, n-1 \\ n \end{cases}, \quad (3)$$

while in the following m layers they assume the values

$$c_{\text{Co}}^p = \begin{cases} 1-c \\ 0 \\ 1-c \end{cases}, \quad c_{\text{Pd}}^p = \begin{cases} c \\ 1 \\ c \end{cases}, \\ p = \begin{cases} n+1 \\ n+2, \dots, n+m-1 \\ n+m \end{cases}. \quad (4)$$

This sequence of concentrations is then repeated r times, *i.e.*, the total number of layers to be summed over in equation (1) is given by $N = r(n+m)$. Clearly enough the simplest case arises when $n = m = 1$:

$$c_{\text{Co}}^p = \begin{cases} c \\ 1-c \\ c \\ 1-c \\ c \\ 1-c \\ \vdots \end{cases}, \quad c_{\text{Pd}}^p = \begin{cases} 1-c \\ c \\ 1-c \\ c \\ 1-c \\ c \\ \vdots \end{cases}, \quad p = \begin{cases} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ \vdots \end{cases}, \quad (5)$$

then for $c = 0.5$ a total of N homogeneously equiconcentrated layers forms the multilayer, while for $c = 1$ one obtains an ordered superstructure on top of the substrate. If the total number of layers N is even, this superstructure is Pd terminated, for odd N the top layer is formed by Co. Summarizing, the kind of disorder defined in equation (5) by the Co concentration in odd numbered layers c , $0.5 \leq c \leq 1$, then c takes on the meaning of an order parameter ($c = 1$, ordered structure), while $c_d = 1 - c$, $0 \leq c_d \leq 0.5$, can be viewed as an ‘‘interdiffusion concentration’’ ($c_d = 0$, no interdiffusion).

Very often when displaying $\Delta E_b(r)$, namely the band energy contribution to the magnetic anisotropy energy for a given number of repetitions as a function of repetitions, one finds an almost linear behavior with respect to r ,

$$\Delta E_b(r) \sim kr + d, \quad (6)$$

which in turn implies that for a sufficiently large number of repetitions, say R , $\Delta E_b(r)/r$ tends to a constant:

$$\lim_{r \rightarrow R} \left(\frac{\Delta E_b(r)}{r} \right) \sim k. \quad (7)$$

Clearly enough, a large positive k is the main object of interest for technological applications of repeated magnetic multilayers such as superstructures of Co with Pd or Pt on top of a suitable substrate.

Before closing this section it should be mentioned that because a fully relativistic approach, *i.e.*, the Dirac equation in the presence of an exchange field, is applied in using the (magnetic) force theorem there is no need to discuss ‘‘correction terms’’ arising from an application of the so-called torque formula (see in particular the discussion in Ref. [16]) which frequently is employed in Pauli-Schrödinger types of approaches.

3 Results

Our results show that only Co/Pd superstructures on a Pd(111) substrate show perpendicular magnetism. Therefore, in our analysis of the two types of substrates considered much more weight is given to the discussion of the results for Co/Pd superstructures along the (111) surface normal.

In the left panels of Figure 1 the band energy contribution to the magnetic anisotropy energy is shown for (Co_nPd_m) superstructures on Pd(111) for a given n with respect to m , while in the right panels m is kept fixed and n varies. From Figure 1 it is easily seen that in terms of a large positive ΔE_b , Co_1Pd_m and Co_3Pd_m superstructures are favored and that when varying the number of Co layers (right) the by now typical oscillations with respect to n set in. These oscillations cause ΔE_b to be particularly small for superstructures of the type Co_2Pd_m .

Figure 2 shows $\Delta E_b(r)$ and $\Delta E_b(r)/r$ for r times repeated superstructures of Co_1Pd_1 (left) and Co_3Pd_1 (right) on Pd(111). In both cases $\Delta E_b(r)$ grows linearly with r , however, for a large number of repetitions,

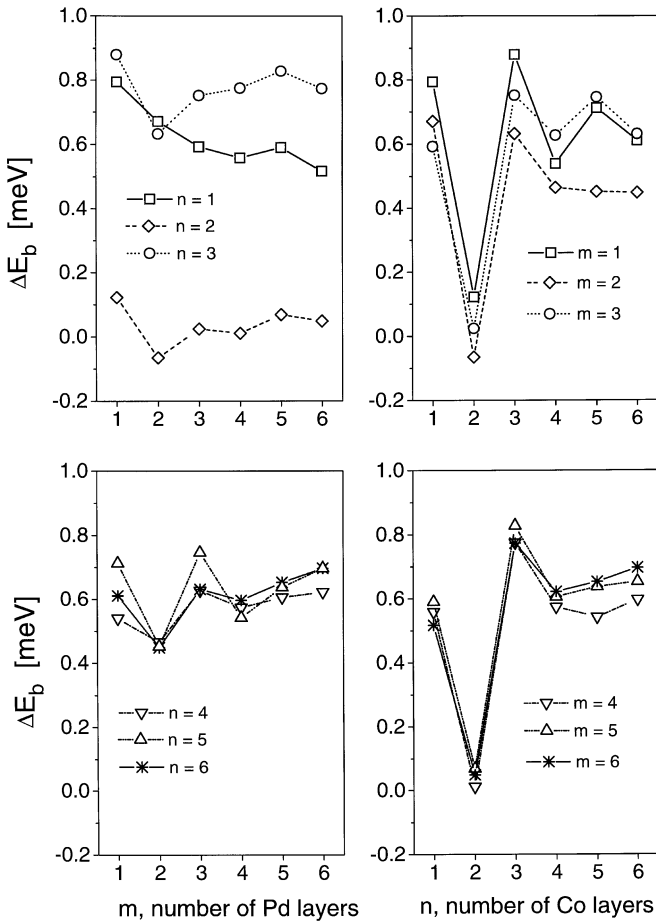


Fig. 1. Band energy contribution to the magnetic anisotropy energy of (Co_nPd_m) superstructures on Pd(111) for a given n with respect to m (left panels) and a given m with respect to n (right panels).

$\Delta E_b(r)/r$ for Co_1Pd_1 superstructures tends to a constant that is more than twice as big as the one for Co_3Pd_1 superstructures, although $\Delta E_b(r=1)$ is larger in the latter case. Clearly enough this kind of behavior can not be read off considering only the $r=1$ cases shown in Figure 1. For repeated superstructures of Co_5Pd_1 on Pd(111) (not shown in here) the corresponding constant k in equation (7) turns out to be substantially smaller than the one for Co_3Pd_1 . This is even more striking, if one normalizes the value of k per atomic layer, which is proportional to a normalization per layer unit volume, since in this case the constants k to be read off Figure 2 have to be divided by two and four for Co_1Pd_1 and Co_3Pd_1 , respectively. Thus, in terms of an optimization of $\Delta E_b(r)/r$ with respect to “large perpendicular magnetism” (large positive magnetic anisotropy energies) repeated Co_1Pd_1 superstructures would obviously be the best choice, if it would not be for interdiffusion effects.

In order to show these effects ΔE_b for an interdiffused Co_1Pd_1 superstructure repeated five times is plotted in Figure 3 as a function of the order parameter c . It should be recalled from equation (5) that for $c=0.5$ this system

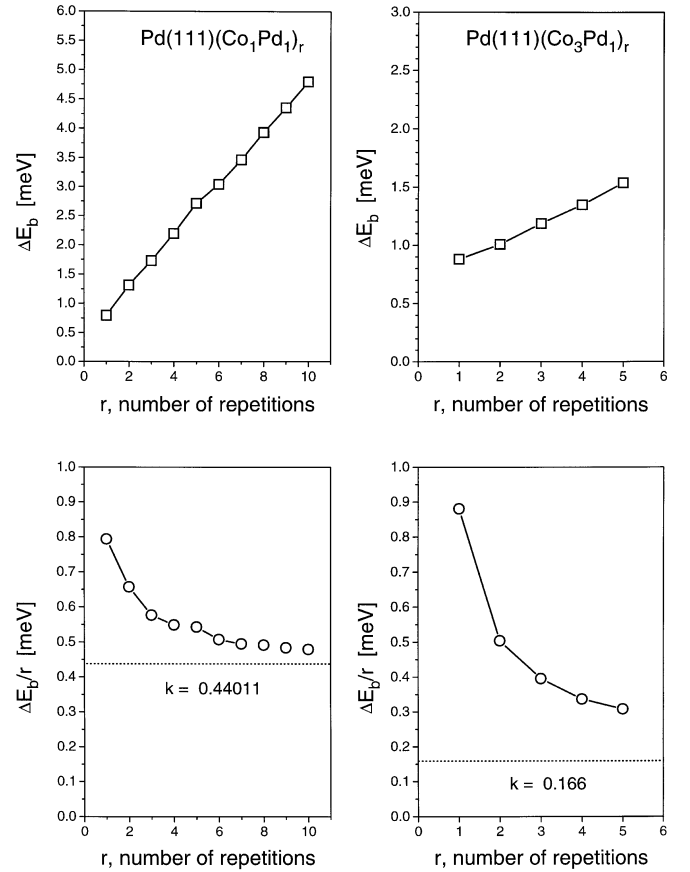


Fig. 2. Band energy contribution (top) to the magnetic anisotropy energy of (Co_nPd_m) superstructures on Pd(111), $n=m=1$ (left) and $n=3, m=1$ (right), as a function of the repetitions r . The bottom shows the band energy contribution per repetition together with the constant k defined in equation (6).

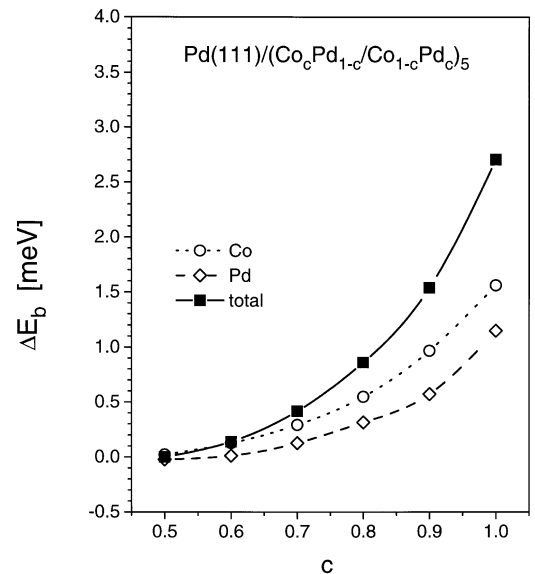


Fig. 3. Band energy contribution (squares) to the magnetic anisotropy energy of interdiffused $(\text{Co}_1\text{Pd}_1)_5$ superstructure on Pd(111) as a function of c . Also shown are the Co- (circles) and Pd-like (diamonds) contributions.

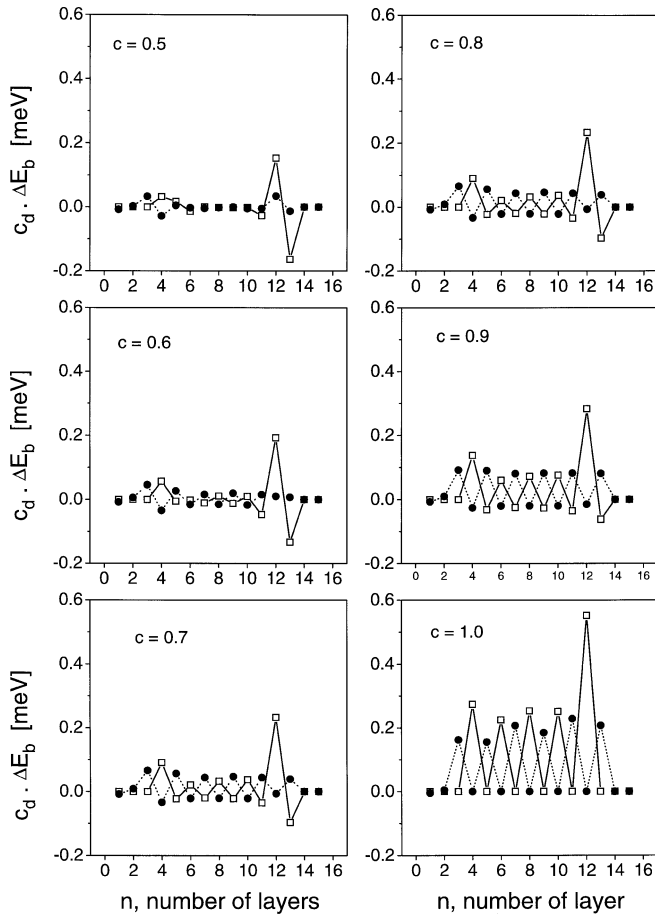


Fig. 4. Component- and layer-resolved band energy contributions to the magnetic anisotropy energy of interdiffused $(\text{Co}_1\text{Pd}_1)_5$ superstructure on Pd(111). It should be noted that for a better visualization of the effects to be seen, the quantities $c_d^p \Delta E_b^p$ are displayed. In here, open squares refer to Co, full circles to Pd, and full squares to the first two vacuum layers.

consists of 10 layers of a (homogeneously) statistically disordered $\text{Co}_{0.5}\text{Pd}_{0.5}$ alloy on top of Pd(111), while $c = 1$ refers to the ordered superstructure $(\text{Co}_1\text{Pd}_1)_5$ (see also the corresponding entry in Fig. 2). From Figure 3 one can see that effects of interdiffusion are indeed dramatic: an admixture of only 10% ($c_d = 0.1$, $c = 0.9$) of Co to the Pd layers (and *vice versa*) already almost halves ΔE_b , and for the homogeneous alloy ($c = c_d = 0.5$) ΔE_b is very close to zero. Interestingly enough the Pd contribution to ΔE_b is nearly as big as that of Co.

In Figure 4 the concentration-weighted layer- and component-resolved contributions to the band energy, namely $c_d^p \Delta E_b^p$, see also equation (1), are displayed. In this figure the first three entries to the left refer to the Pd buffer, *i.e.*, to the Pd layers joining up to the semi-infinite Pd substrate, the last two ones to vacuum layers. Following the various situations with increasing c (increasing ordering) one can see that the Co contribution first shows a strong oscillation close to the surface, the negative part of it decreases with increasing ordering: the negative contribution from the surface layer seen for high disorder is a

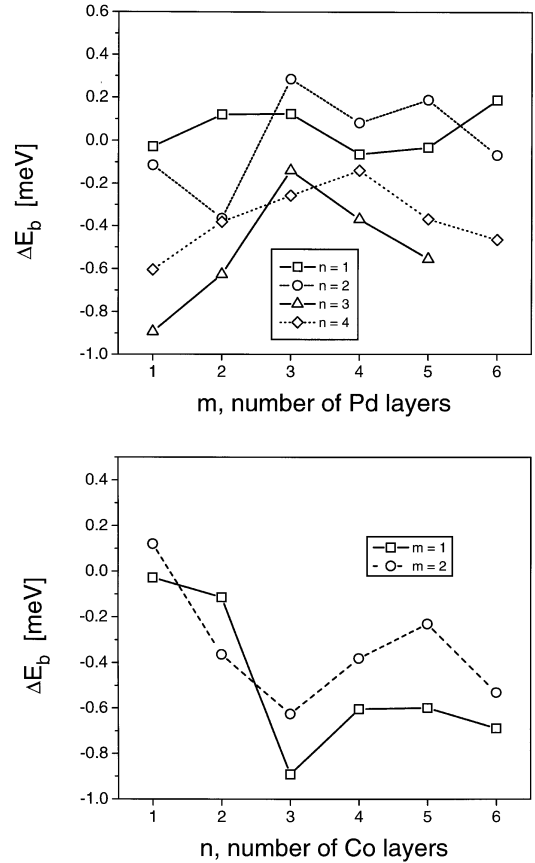


Fig. 5. Band energy contribution to the magnetic anisotropy energy of (Co_nPd_m) superstructures on Pd(100) for a given n with respect to m (top) and for a given m with respect to n (bottom).

Co-like contribution. For $c \geq 0.7$ both Co and Pd contributions are characterized by oscillations with a period of two. The strong positive contribution to ΔE_b in layer 12, which in the ordered structure refers to the Co layer closest to the surface, gains considerably weight as the degree of ordering increases. In fact, it is mostly the contribution from this particular layer that makes the Co contribution in Figure 3 bigger than the Pd contribution. In the interior of the multilayer, *i.e.*, about two layers off the respective interfaces to the vacuum and to the bulk, independent of the degree of ordering the corresponding contributions from Co- and Pd-rich layers are of about the same value.

Turning now to the results for the Pd(100) substrate, one can see from Figure 5 that for this surface orientation the occurrence of perpendicular magnetism is very unlikely: only in very few cases ΔE_b is positive (top). Increasing the number of Co layers, see Figure 5 (bottom), immediately causes ΔE_b to turn negative. Since the magnetic dipole-dipole interaction is always negative and scales linearly with the thickness of the magnetic multilayer, Co_nPd_m superstructures on Pd(100) have to be ruled out as perpendicular magnets. This negative finding is certainly amplified when considering repetitions of such superstructures. Figure 6 shows $\Delta E_b(r)$ and $\Delta E_b(r)/r$ for

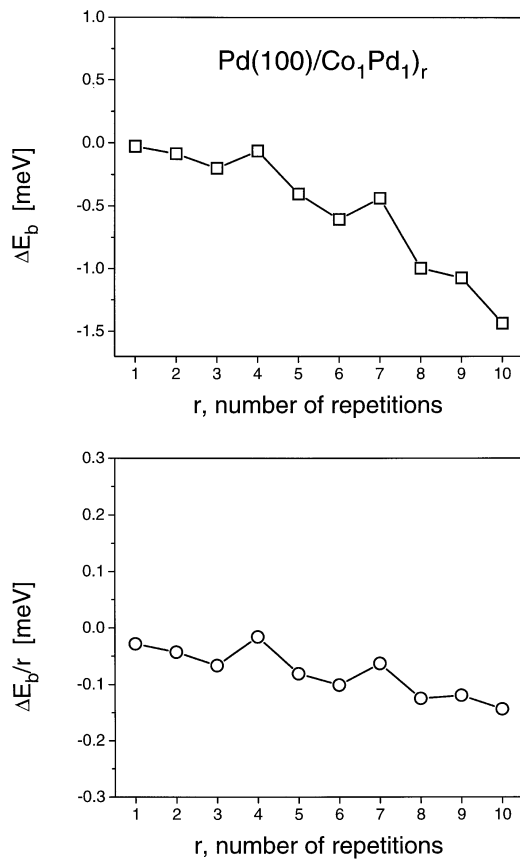


Fig. 6. Band energy contribution (top) to the magnetic anisotropy energy of (Co_nPd_m) superstructures on Pd(100), $n = m = 1$, as a function of the repetitions r . The bottom shows the band energy contribution per repetition.

r times repeated superstructures of Co_1Pd_1 on Pd(100). As can be seen *-grasso modo-* with an increasing number of repetitions $\Delta E_b(r)$ becomes more negative, although $\Delta E_b(r)$ does not vary strictly linearly with r . An oscillation with a period of 4 seems to modify an almost linear decrease of $\Delta E_b(r)$ with respect to r .

Let us finally briefly characterize the layer-resolved spin and the orbital magnetic moments for the superstructures considered in this paper. Generally we can say, that in all $(\text{Co}_n\text{Pd}_m)_r$ superstructures the spin moments are close to $2 \mu_B$ for Co and to $0.3 \mu_B$ for Pd, while the orbital moments are $0.13\text{-}0.14 \mu_B$ and $0.03\text{-}0.04 \mu_B$ for Pd. It is worthwhile to note that the so-called Pd buffer layers, which have to be regarded as the top three layers of the substrate, are magnetically active. This kind of feature is typical also for Pd caps. Interestingly enough, the Co_nPd_m superstructures on Pd(100) and Pd(111) show different characteristic variations of the spin moment in the Pd_m cap, namely, the fall off in direction of the surface is slower in the case of the (111) than in the (100) surface direction.

4 Comparison with experiment

In a series of two papers Engel *et al.* [2,3] investigated the magnetic properties and the magnetic anisotropy in epitaxial CoPd “superlattices” on Pd substrates. In particular they carried out measurements with samples of the type $(x \text{ \AA} \text{ Co}/10 \pm 1 \text{ \AA} \text{ Pd})$, $2 \leq x \leq 20$, deposited on a thick layer of Pd. In the case of epitaxial growth along (111) they find a large perpendicular anisotropy and a reorientation transition to an in-plane orientation of the magnetization for x larger than 24. “In sharp contrast to the (111) orientation”, as they state in [3], “the (001) superlattices show a cross-over to in-plane behavior between one and two atomic layers of Co”. The latter fact was already reported in an earlier paper on Co/Pd superstructures grown on NaCl [1]. In [1] as well as in [3] a “large enhancement” is reported for (100) as well as for (111) oriented superstructures of Co/Pd. Since $10 \pm 1 \text{ \AA} \text{ Pd}$ correspond to about 5–6 layers of Pd in the case of a Pd(111) substrate direct comparison can be made to Figure 1: at $m = 6$ all ΔE_b are positive, in particular when considering not too thin Co slabs ($n \geq 3$).

Without considering the actual values of the magnetic dipole-dipole contribution, ΔE_{dd} , the last entry in Figure 1b, showing the variation of ΔE_b for (Co_nPd_m) , $m = 6$, with respect to n , clearly confirms the experimental observations made, in particular since in the experiment the smallest Co-slab thickness is about 2.5 \AA , which rather refers to 3 monolayers than to 2 monolayers of Co. Figure 5 (bottom) on the other hand gives an impressive account of the fact found experimentally that in Co/Pd superstructures on Pd(100) the magnetization is in-plane. In a more recent paper [4] the magnetic properties of repeated multilayers of the type $(x \text{ \AA} \text{ Co}/10 \text{ \AA} \text{ Pd})_{10}$, $2 \leq x \leq 4$ were reported. However, since these systems were grown on a glass substrate, no direct comparison to the present theoretical results can be made. Figure 4 shows the long reaching tail of induced magnetic moments in the Pd cap describing in a quantitative manner the “large enhancement of the magnetization arising from Pd polarization” seen experimentally.

Turning now to the results for the interdiffused superstructures, Figures 3 and 4, it is evident that a direct comparison to measured anisotropy constants has to be handled with extreme care. Not only that interdiffusion can immediately decrease a large positive magnetic anisotropy (Fig. 3), but also a clear distinction between a “volume-like” and an “interface-like” contribution to the magnetic anisotropy energy cannot be given, since from Figure 4 it follows that a partitioning of the sum over layerwise contributions into partial sums, see also equation (1), necessarily must be somewhat arbitrary [18,19,22].

5 Summary

In the present paper it is shown that in contrast to a Pd(100) substrate on which $(\text{Co}_n\text{Pd}_m)_r$ superstructures always show an in-plane orientation of the magnetization, on a Pd(111) substrate the magnetization of such

superstructures is perpendicularly oriented. In considering repeated $(\text{Co}_n\text{Pd}_m)_r$ superstructures on Pd(111) it is found that the largest effects correspond to $n = m = 1$. For increasing n the band energy contribution to the anisotropy energy per repetition decreases. As in the case of Co/Pt superstructures [19, 22] interdiffusion can play a decisive role in determining the actual size of the magnetic anisotropy energy. In particular it was shown that interdiffusion of less than 10% can reduce the magnetic anisotropy energy considerably.

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