Spin moments, orbital moments and magnetic anisotropy of finite-length Co wires deposited on Pd(110)

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*New Journal of Physics* 4 (2002) 100.1–100.14 (http://www.njp.org/)
Received 13 November 2002
Published 17 December 2002

**Abstract.** The ground-state spin moments \(\langle S_z \rangle\), orbital moments \(\langle L_z \rangle\) and magnetic anisotropy energy (MAE) of Co\(_N\) one-dimensional (1D) clusters (\(N \leq 12\)) deposited on the Pd(110) surface are determined in the framework of a self-consistent, real-space tight-binding method. Remarkably large total magnetic moments per Co atom, \(M_z = (2\langle S_z \rangle + \langle L_z \rangle)/N = 2.8–2.9\ \mu_B\), are obtained, which can be understood as the result of three physically distinct effects. The first and leading contribution is given by the local spin moments \(\langle S_{iz} \rangle\) at the Co atoms \(i = 1, N\) \(2\langle S_{iz} \rangle_{\text{Co}} \simeq 1.6\ \mu_B\). Second, significant spin moments are induced at the Pd atoms \(i > N\) close to the Co–Pd interface, which amount to about 25% of \(M_z\) \(2\langle S_{iz} \rangle_{\text{Pd}} = 0.2–0.3\ \mu_B\). Finally, enhanced orbital magnetic moments \(\langle L_{iz} \rangle\) are responsible for approximately 20% of \(M_z\). In the case of the Co atoms, \(\langle L_{iz} \rangle_{\text{Co}} = 0.28–0.33\ \mu_B\) is almost a factor of three larger than the Co bulk orbital moment, while in Pd atoms \(\langle L_{iz} \rangle_{\text{Pd}} = 0.05\ \mu_B\) represents about 15% of the total local moment \(\mu_{iz} = 2\langle S_{iz} \rangle + \langle L_{iz} \rangle\). These results and the associated MAEs are analysed from a local perspective. The role of the cluster–surface interactions is discussed by comparison with the corresponding results for free-standing wires. Particularly in the case of monatomic 1D Co chains we observe that the lowest-energy magnetization direction (easy axis) changes from in line to off plane upon deposition on Pd(110). Wire–substrate hybridizations are therefore crucial for the magneto-anisotropic behaviour of 1D magnetic nanostructures on metallic substrates.
1. Introduction

Nanostructured magnetic materials involving transition metals (TMs) are the subject of an extraordinary research activity which is driven by both fundamental and practical interests [1]–[16]. A particularly attractive feature of these systems is the strong sensitivity of their electronic and magnetic properties to the geometrical and chemical environment of the atoms. Consequently, numerous experimental studies have been concerned with the production and characterization of nanometre-scale magnetic materials involving TMs and noble metals in different structural arrangements. Experimental achievements, such as atomic manipulation using a scanning tunnel microscope [17] or diffusion controlled aggregation [18], allow a controlled formation of diverse low-dimensional nanostructures at surfaces, including chains and islands of variable length and width. In this way, new metastable states of matter are accessible, which open the possibility of novel investigations in the vast field of sub-monolayer magnetism [9]–[16]. These developments also reinforce the interest in theoretical studies that provide us with a microscopic understanding of observed specific properties or with predictions of as yet unknown phenomena.

Two of the main characteristics of a magnetic material are the ground-state magnetic moments, which define the saturation magnetization, and the magnetic anisotropy energy (MAE), which determines the low-temperature orientation of the magnetization $\vec{M}$ and the stability of the magnetization direction. On the one hand, the sources of magnetism are the currents associated to the electronic motion, or orbital moments, and the electron’s intrinsic spin. On the other hand, the dependence of the electronic structure and magnetic properties on the orientation of $\vec{M}$ is dominated by the spin–orbit (SO) interactions. In particular, the MAE—defined as the energy difference involved in changing $\vec{M}$ from the low-energy direction, or easy axis, to a high-energy direction, or hard axis—is a magnitude of crucial importance in view of technological applications like magnetic recording or memory devices, where $\vec{M}$ must be pinned to a given direction in space. The control and understanding of these properties at a microscopic level are central to the development of magnetic nanostructures at surfaces.

Symmetry and dimensionality are known to play a major role in determining the magnetic properties of TM systems. Let us recall for instance the remarkable enhancement of spin moments, orbital moments and MAE upon going from the solid to two-dimensional (2D) thin films, surfaces and interfaces [19], or the appearance of remarkable in-plane MAEs in cases of low symmetry within the film or surface plane [20, 21]. It is therefore quite reasonable to expect that a further reduction of the system dimensions, on the way from two- to one-dimensional (1D) structures, should result in new effects, which are most interesting from a fundamental point of view and which could be very important for potential applications. Consequently, the interest in wires and 1D nanostructures deposited on surfaces is growing steadily [9]–[16]. For instance, recent experiments on Co wires grown at the steps of the Pt(997) surface have revealed remarkably enhanced Co orbital magnetic moments, which are largest for the monatomic chains, and which decrease rapidly with chain width approaching typical monolayer values already for the biatomic chain [16].

Several theoretical studies have already been concerned with this problem [22]–[26]. For example, in the simplest free-standing geometry the infinite-length monatomic chains have been shown to present very large orbital magnetic moments and MAEs, which are in general far more important than in thin films or small compact clusters. This effect is further enhanced in finite-length chains, which are the TM systems showing the largest MAEs we are aware of [22].
the case of wires deposited on metallic surfaces one faces a more complex situation since the magnetic atoms experience both the reduction of dimensionality as in free-standing or nearly isolated wires, as well as the interactions with the substrate, which often result in some degree of loss of 1D character [22]. A variety of interesting magnetic behaviours result from these competing effects, as demonstrated by recent measurements and theoretical calculations of spin moments, orbital moments and MAE of Fe, Co and 4d and 5d TM wires on Cu, Ag, Pd, Pt and Au surfaces [22]–[28].

The purpose of this paper is to investigate the magnetic and electronic properties of finite-length Co wires deposited on the Pd(110) surface. This specific problem is expected to be particularly interesting due to the strong magnetic susceptibility of Pd as a nonmagnetic substrate, and since the Co/Pd interfaces are known to show a remarkably rich magneto-anisotropic behaviour [20, 29]. Indeed, thin Pd-capped Co films deposited on Pd(111) have been shown to present a stable magnetization direction along the surface normal. It is therefore very appealing, from both fundamental and technological standpoints, to investigate the possibility of tailoring the morphology of Co nanostructures on Pd in order to stabilize a perpendicular magnetic anisotropy, which could be useful in high-density recording and magneto-optical devices [30]–[32].

The remainder of the paper is organized as follows. In the next section the self-consistent tight-binding (SCTB) method used for the calculations is briefly recalled. Further details and other applications to TM clusters, thin films and surfaces may be found in [21, 22, 33]–[35]. Results for the spin moments, orbital moments and MAEs of $\text{Co}_N$ wires on Pd(110) with $N \leq 12$ atoms are presented and discussed in section 3. The different local contributions to the magnetic properties are analysed, and the behaviours of free and deposited wires are contrasted. Finally, section 4 summarizes the main conclusions.

2. Theoretical method

The redistributions of the spin-polarized electronic density associated with the changes in local coordination number and geometrical atomic arrangements play a central role in low-dimensional itinerant magnetism. Local approaches to the theory of electronic structure have been proved to be most successful in this context, since they allow us to relate the electronic properties to the local environments of the atoms in a transparent way [36, 37]. An efficient method of taking into account the system-specific changes in the spin-density distribution is provided by the SCTB approach proposed in [33] as extended to include SO interactions [34, 35]. This theory allows study of finite and extended systems having a reduced or lack of translational symmetry, since the local densities of electronic states are computed by means of a real-space recursion expansion [38]. In the case of TM nanostructures, the magnetic properties are dominated by the contribution of the d-electron states, particularly concerning the orbital magnetic moments and the MAEs, which are the main subjects of this work. Consequently, in the present study we focus on the d-electron Hamiltonian given by [34, 35]

$$H = H_0 + H_C + H_{SO}.$$  

The inter-atomic hopping term is

$$H_0 = \sum_{\langle i,j \rangle, \alpha, \beta, \sigma} t^{\alpha \beta}_{ij} \hat{c}^\dagger_{i\alpha\sigma} \hat{c}_{j\beta\sigma},$$  

(1)

(2)
where $\hat{c}_{i\alpha\sigma}^\dagger$ ($\hat{c}_{i\alpha\sigma}$) refers to the creation (annihilation) operator of an electron with spin $\sigma$ at the d orbital $\alpha$ of atomic site $i$, and $t_{ij}^{\alpha\beta}$ denotes the corresponding hopping integrals. The Coulomb interaction term $H_C$ is treated in the unrestricted Hartree–Fock approximation:

$$H_C = \sum_{i\alpha\sigma} \Delta \varepsilon_{i\sigma} \hat{n}_{i\alpha\sigma},$$

(3)

where $\hat{n}_{i\alpha\sigma} = \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{i\alpha\sigma}$ is the electron number operator and $\Delta \varepsilon_{i\sigma} = U \Delta n(i) - \sigma J \langle S_{i\delta} \rangle$ is the site- and spin-dependent shift of the d level $\varepsilon_{i\sigma} = \varepsilon_d^0 + \Delta \varepsilon_{i\sigma}$. Here, $\varepsilon_d^0$ stands for the d-orbital energy in the paramagnetic bulk ($\Delta n(i) = n(i) - n_d$(bulk)), $U$ for the average direct Coulomb-repulsion integral and $J$ for the average exchange integral. The spin-quantization axis $\delta$ is taken to be parallel to the magnetization direction, which is assumed to be uniform throughout the wire. The third term in equation (1) is the SO interaction

$$H_{SO} = -\sum_{i,\alpha\sigma,\beta\sigma'} \xi_i (\vec{L}_i \cdot \vec{S}_i)_{\alpha\beta\sigma\sigma'} \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{i\beta\sigma'},$$

(4)

which is treated in the usual intra-atomic approximation [39]. $\xi_i$ stands for the SO coupling constant at atom $i$ (e.g. $\xi_i = \xi_{Pd}$ or $\xi_{Co}$) and $(\vec{L}_i \cdot \vec{S}_i)_{\alpha\beta\sigma\sigma'}$ refer to the intra-atomic matrix elements of $\vec{L} \cdot \vec{S}$ that couple the up and down spin manifolds depending on the relative orientation of the magnetization with respect to the lattice structure.

The average d-electron occupation at site $i$,

$$n(i) = \sum_{\alpha} \langle \hat{n}_{i\alpha\uparrow} \rangle + \langle \hat{n}_{i\alpha\downarrow} \rangle,$$

(5)

and the local spin magnetic moment,

$$\langle S_{i\delta} \rangle = \frac{1}{2} \sum_{\alpha} \langle \hat{n}_{i\alpha\uparrow} \rangle - \langle \hat{n}_{i\alpha\downarrow} \rangle,$$

(6)

are calculated self-consistently by integrating the local densities of states (LDOSs) $\rho^{\delta}_{i\alpha\sigma}(\varepsilon) = -(1/\pi) \text{Im} \{ G_{i\alpha\sigma,i\alpha\sigma}(\varepsilon) \}$ up to the Fermi energy $\varepsilon_F$ of the substrate. Here, $G(\varepsilon) = [\varepsilon - H]^{-1}$ refers to the Green function operator. Since the $\rho^{\delta}_{i\alpha\sigma}$ depend on the magnetization direction $\delta$, they are determined by performing independent self-consistent calculations for each orientation of $\vec{M}$. In practice, the $\rho^{\delta}_{i\alpha\sigma}(\varepsilon)$ are computed by using the Haydock–Heine–Kelly recursion method [38].

The number of levels $K$ of the continued fraction expansion is systematically increased until the results become independent of $K$. For the calculation reported here $K = 20–25$ fulfils this condition. All these recursion coefficients are determined exactly without any spurious boundary effects. Therefore, a large number of atoms (about 50 000) is involved in the present real-space calculations. In this way the effects of hopping, Coulomb and SO interactions are treated on the same footing.

Once self-consistency is achieved, the average local orbital moments $\langle L_{i\delta} \rangle$ at atom $i$ are calculated from

$$\langle L_{i\delta} \rangle = \sum_{\sigma} \sum_{m=-2}^{2} \int_{-\infty}^{\varepsilon_F} m \rho^{\delta}_{i\alpha\sigma}(\varepsilon) \, d\varepsilon,$$

(7)

where $m$ indicates the magnetic quantum number. The quantization axis of the orbital momentum is thereby taken to be the same as the spin quantization axis. The electronic energy $E_\delta(i) = \sum_\delta E_\delta(i)$ can be written as the sum of local contributions

$$E_\delta(i) = \sum_{\alpha\sigma} \left[ \int_{-\infty}^{\varepsilon_F} \varepsilon \rho^{\delta}_{i\alpha\sigma}(\varepsilon) \, d\varepsilon - E^{\text{dc}}_{i\alpha\sigma} \right]$$

(8)
corresponding to the different atoms $i$ of the deposited cluster and its environment. Here $E_{\text{dc}}^{\text{ia}} = (1/2)\Delta\varepsilon_{ia}\langle n_{ia}\rangle$ stands for the double-counting correction. The MAE is defined as the change $\Delta E$ in the electronic energy $E_{\delta}$ associated with a change in the orientation of the magnetization. In this work, we consider the direction $\delta = z$ perpendicular to the surface ($\hat{\delta} = (1, 1, 0)/\sqrt{2}$) and two directions within the surface plane, the direction $\delta = x$ along a nearest-neighbour (NN) bond ($\hat{\delta} = (1, -1, 0)/\sqrt{2}$), and $\delta = y$ perpendicular to $\hat{x}$ ($\hat{\delta} = (0, 0, 1)$). Thus, positive (negative) values of the off-plane anisotropy energy $\Delta E_{xz} = E_x - E_z$ indicate a perpendicular easy (hard) axis. Taking advantage of the local formulation one may express $\Delta E_{xz} = \sum_i \Delta E_{xz}(i)$ as a sum of atom-resolved contributions

$$\Delta E_{xz}(i) = E_x(i) - E_z(i),$$

where $E_{\delta}(i)$ are given by equation (8). Thus, the magneto-anisotropic properties can be related to the various local atomic environments. Analogous expressions hold for the in-plane anisotropy energy $\Delta E_{xy} = E_x - E_y$. Notice that the calculation of $\Delta E$ as the difference of $E_{\delta}$ is a non-perturbative approach that includes in particular the anisotropic effects of spin-density redistributions resulting from SO interactions. This requires a very precise determination of $E_{\delta}$ and of the self-consistent equations, since $\Delta E$ is usually a small quantity of the order of a millielectron volt. For these reasons we use a mixed spin–orbital basis, which assures a high numerical stability of $\Delta E$ with moderate number of recursion coefficients.

3. Results and discussion

The parameters used for the calculations are specified as follows. The two-centre hopping integrals are given by the canonical expression in terms of the corresponding bulk band widths [22]. The intra-atomic d-electron exchange integral $J$ of Co yields the proper magnetic moment and exchange splitting in the solid ($J_{\text{Co}} = 0.76 \text{ eV}$). For Pd, which is non-magnetic in the bulk, $J$ is derived from local spin-density calculations ($J_{\text{Pd}} = 0.52 \text{ eV}$) [41]. The values of the SO-coupling constant $\xi$ are obtained from [39] ($\xi_{\text{Co}} = 88 \text{ meV}$ and $\xi_{\text{Pd}} = 200 \text{ meV}$). Concerning the Co$_N$ structure and absorption position, we consider 1D monatomic and biatomic chains deposited along the $(1, -1, 0)$ valleys of the Pd$(1, 1, 0)$ surface. This is illustrated in figures 1 and 2. The vertical Co–Pd interlayer distance is taken as the average between the $d_{\text{Co–Co}}$ (bulk) and $d_{\text{Pd–Pd}}$ (bulk). Relaxation effects are discussed in section 3.2.

3.1. Spin and orbital moments

Table 1 reports the average magnetic moments per Co atom in Co$_N$ wires. For each considered size $N$ the spin, orbital and total moments corresponding to three different situations are given: the deposited Co wire on Pd(110) including the contributions of the Pd-substrate atoms, the deposited Co wire as in the preceding case but taking into account only the magnetic contributions of the Co atoms (values in curved brackets), and finally the case of free-standing wires having the same inter-atomic distance as the deposited ones but without any hybridization with the substrate (values in square brackets). The modulus of the spin moments $\langle \hat{S} \rangle$ is found to depend very weakly on the direction $\delta$ of the magnetization (typically $|\langle S_z \rangle - \langle S_x \rangle| \approx 10^{-4} - 10^{-3} \mu_B$), as in previous studies on films or free clusters. Therefore, only the results for one magnetization direction $\langle S_z \rangle$ are shown. In contrast, the anisotropy of the orbital moments $\langle L_\delta \rangle$ is far more

† Dipole–dipole interactions are quantitatively unimportant for the small systems considered in this paper.
Figure 1. Illustration of a monatomic Co_N chain deposited on Pd(110) and of the magnetization directions considered in the calculations. The z direction is perpendicular to the xy surface plane. Open (filled) circles refer to Pd (Co) atoms. The numbers label the different atomic sites i for N = 6.

Figure 2. Illustration of a biatomic Co_N chain deposited on Pd(110) as in figure 1. Open (filled) circles refer to Pd (Co) atoms. The numbers label the different atomic sites i for N = 12.

important. Values of \(|\langle L_z \rangle - \langle L_x \rangle| \approx 0.1-0.2 \mu_B\) are not uncommon. Thus, the reported total magnetizations M_{\delta_0} refer to the magnetization direction \(\delta_0\) yielding the lowest energy (easy axis).

First of all, one observes that the total magnetic moments per Co atom M_{\delta_0} of the deposited monatomic chains are remarkably large for all the considered sizes (N \leq 10). Notice that the M_{\delta_0} appear to depend very weakly on N in the considered size range: M_z = 2.85, 2.88 and 2.86 \mu_B for N = 3, 4 and 10, respectively. Moreover, the results for the ten-atom chain are actually not far from the infinite-length limit for which we obtain M_z = 2.86 \mu_B. Comparison with free-standing chains shows that the wire–substrate interactions yield a significant enhancement of the magnetic moments per Co atom. For instance, in Co_4 and Co_10, M_{\delta_0} changes from 2.88 and 2.86 \mu_B to 2.54 and 2.58 \mu_B, respectively, as we switch off the hybridizations with the surface keeping the structure unchanged. This trend holds for almost all chains considered; the only
Table 1. Magnetic properties of CoN wires on Pd(110) (N \leq 12). The averages per Co atom of the spin magnetic moment \(2\langle S_z \rangle\), the orbital magnetic moments \(\langle L_\delta \rangle\) for \(\delta = x, y\) and \(z\) and the total magnetic moment \(M_\delta_0 = 2\langle S_{\delta_0} \rangle + \langle L_{\delta_0} \rangle\) along the easy axis \(\delta_0\) are given in Bohr magnetons (\(|S_z - S_x| \sim 10^{-3} \mu_B\)). The results correspond to monatomic chains for \(N \leq 10\) (see figure 1) and to a biatomic chain for \(N = 12\) (see figure 2). For each \(N\), the first line (second line in curved brackets) refers to deposited wires including (excluding) the contributions of the Pd atoms at the Co–Pd interface. The values in square brackets apply to free-standing CoN chains having the same structure as the deposited ones.

| \(N\) | \(2\langle S_z \rangle\) | \(\langle L_x \rangle\) | \(\langle L_y \rangle\) | \(\langle L_z \rangle\) | \(M_{\delta_0}\) | \(\delta_0\) |
|------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 3    | 2.43            | 0.42            | 0.42            | 2.85            | \(z\)           | (1.63) \[1.69\] |
|      | (0.33)          | (0.30)          | (0.28)          | (1.91)          | (z)             | [0.33] \[1.00\] |
| 4    | 2.43            | 0.45            | 0.45            | 2.88            | \(z\)           | (1.64) \[1.69\] |
|      | (0.34)          | (0.30)          | (0.28)          | (1.92)          | (z)             | [0.34] \[0.69\] |
| 6    | 2.42            | 0.42            | 0.43            | 2.85            | \(z\)           | (1.64) \[1.69\] |
|      | (0.33)          | (0.30)          | (0.28)          | (1.92)          | (z)             | [0.33] \[0.71\] |
| 10   | 2.43            | 0.43            | 0.43            | 2.86            | \(z\)           | (1.64) \[1.69\] |
|      | (0.33)          | (0.33)          | (0.28)          | (1.92)          | (z)             | [0.33] \[0.66\] |
| 12   | 2.37            | 0.41            | 0.39            | 2.78            | \(y\)           | (1.65) \[1.69\] |
|      | (0.31)          | (0.29)          | (0.27)          | (1.94)          | \(y\)           | [0.31] \[2.58\] |

The enhancement of \(M_{\delta_0}\) after deposition is largely dominated by the contributions of the magnetic moments induced at the Pd atoms of the Co–Pd interface. This is more clearly demonstrated by comparing the total \(M_{\delta_0}\) of deposited clusters with the contribution of the Co atoms alone (see values in curved brackets in table 1). For instance, in the Co\(_4\) chain, the Co part of \(M_{\delta_0}\) is 1.92 \(\mu_B\), while including the induced Pd moments it amounts to 2.88 \(\mu_B\). In addition, it is interesting to note that the magnetization of the Pd atoms is not significantly modified by the hybridization with the Pd. In fact, comparison with the results for free Co chains, given in square brackets, shows that deposition on the Pd substrate only results in small reductions of the Co moments. This small effect is then overcompensated by the induced Pd moments yielding enhanced \(M_{\delta_0}\). The remarkable role played by the Pd atoms demonstrates the importance of a precise self-consistent treatment of magnetic–nonmagnetic interfaces, particularly in the case of highly polarizable metallic substrates.

A more detailed analysis of the average spin and orbital moments reported in table 1 reveals that the magnetization \(M_i = (2\langle S_i \rangle + \langle L_i \rangle) / N\) of \(\text{Co}_N\) on Pd(110) can be regarded as the result of three major effects. The first and leading contribution is given by the spin moments at the Co atoms \(i = 1–N\) for which we obtain \(2\langle S_z \rangle_{\text{Co}} = 1.63–1.64 \mu_B\). These depend very weakly on \(N\).
and are somewhat smaller than in the corresponding free chains \(2\langle S_z \rangle_{\text{Co}} = 1.69 \, \mu_B\). Note that the Co spin moments constitute about 58\% of the total magnetization per Co atom. The second important contribution to \(M_\delta\) are the local spin moments induced at the Pd atoms of the Co–Pd interface that amount typically to about 0.80 \(\mu_B\). This corresponds to approximately 49\% of the spin polarization per Co atom and to 28\% of the total moment (see table 1). As previously discussed, these induced spin moments are responsible for most of the enhancement of \(M_\delta\) in deposited wires as compared to the free-standing case. The local magnetic moments at the Co–Pd interface are discussed in more detail in section 3.3. Finally, the third main part of the calculated magnetization is given by the orbital magnetic moments \(\langle L_\delta \rangle\), which are always parallel to the spin moments, as corresponding to elements having a d shell which is more than half filled. Thus, \(\langle L_\delta \rangle\) adds up to \(\langle S_\delta \rangle\) representing about 14\% of \(M_\delta\). It should however be noted that the anisotropy of \(\langle L_\delta \rangle\) is far more important than the one of the spin moments. This anticipates a strong environment dependence for the MAE due to the SO interactions. As in the case of the spin polarization, the largest part of the orbital moments is due to the Co atoms (values in curved brackets). Still, the Pd contributions represent about 28\% of \(\langle L_\delta \rangle\) (see table 1). It is also interesting to observe that the average orbital moments at the Co atoms are significantly enhanced as compared to the corresponding bulk moment \(\langle L_\delta\rangle_{\text{Co-bulk}} \simeq 0.13 \, \mu_B\). Quantitatively, the calculated Co orbital moments along the easy axis \(\delta_0\) are typically \(\langle L_{\delta_0} \rangle = 0.33 \, \mu_B\). These values are somewhat smaller than those observed in experiments on Co chains of various widths (monatomic, biatomic etc, up to the monolayer) grown at the steps of the Pt(997) surface [16]. Comparison with the results for free chains (results in square brackets) shows that the hybridizations with the substrate lead to a strong reduction of the Co orbital moments which can be interpreted as a consequence of the loss of 1D character associated with the induced Pd moments [22].

3.2. Magnetic anisotropy energy

In table 2 results are given for the off-plane MAEs \(\Delta E_{xz} = E_x - E_z\) and \(\Delta E_{yz} = E_y - E_z\), and the in-plane MAE \(\Delta E_{xy} = E_x - E_y\) of Co\(_N\) chains deposited on Pd(110). Results for free chains having the same structure as the deposited ones are also reported for the sake of comparison. The monatomic free-standing chains show an in-line easy axis with remarkably large MAEs per Co atom (\(\Delta E_{xz} < 0\) with \(\vert \Delta E_{xz} \vert = 6.2-20 \, \text{meV}\)). In the case of deposited chains, the interaction with the substrate changes the easy axis from in line to off plane and reduces by an order of magnitude the absolute value of the MAEs. This is consistent with the reduction of the orbital moments discussed in the previous section. Notice that the results for free-standing chains are obtained using the same Co–Co NN distance as in the deposited ones which is equal to the Pd–Pd NN distance \(d_{\text{Pd}} = 2.75 \, \text{Å}\). A bond-length contraction to typical Co–Co NN distances \(d_{\text{Co}} = 2.5 \, \text{Å}\) would result in an important reduction of \(\langle L_\delta \rangle\) and \(\Delta E_{xz}\) even if the interactions with the substrate were neglected (e.g., \(\Delta E_{xz} \simeq 7 \, \text{meV}\) for \(d_{\text{Co}} = 2.5 \, \text{Å}\) and \(N \geq 10\)) [22].

Results for a biatomic Co\(_{12}\) wire are also given in table 2 in order to explore the crossover from 1D to 2D behaviour (see figures 1 and 2). This is a subject of fundamental importance particularly since in some cases it is experimentally possible to vary the width of the deposited chains by changing the aggregation conditions [16]. Important quantitative differences are observed by comparing the results for the monatomic and biatomic chains (e.g., \(N = 6\) and 12). First of all, one should notice that the largest part of the enhancement of the MAE found in the monatomic case disappears in the bichain. In fact, \(\Delta E_{yz} = -0.22 \, \text{meV}\) for \(N = 12\) which
Table 2. MAE per Co atom of $\text{Co}_N$ wires on Pd(110). The off-plane MAEs $E_x - E_z$ and $E_y - E_z$, and the in-plane MAE $E_x - E_y$ are given in millielectron volts. The wires are monatomic for $N \leq 10$ and biatomic for $N = 12$. These and the magnetization directions $x$, $y$ and $z$ are illustrated in figures 1 and 2. Results in square brackets refer to free $\text{Co}_N$ having the same structure as the deposited wires.

| $N$ | $E_x - E_z$ | $E_y - E_z$ | $E_x - E_y$ |
|-----|-------------|-------------|-------------|
| 3   | 2.00        | 1.48        | 0.52        |
|     | [−20.10]    |             |             |
| 4   | 1.42        | 1.21        | 0.21        |
|     | [−6.16]     |             |             |
| 6   | 1.26        | 0.86        | 0.40        |
|     | [−13.59]    |             |             |
| 10  | 1.11        | 0.71        | 0.40        |
|     | [−13.09]    |             |             |
| 12  | 0.20        | −0.22       | 0.42        |

is similar to typical values obtained in thin films. This indicates a quite rapid crossover to the 2D behaviour. In other words the remarkably large anisotropy energies of monatomic wires are intrinsically related to the 1D character, which is also consistent with the reduction of $\Delta E_{yz}$ found upon deposition. Another interesting effect is the change in the easy axis from perpendicular to the Pd surface ($z$ axis) for the monatomic chains to in plane but still perpendicular to the chain ($y$ axis) for the $\text{Co}_{12}$ bichain. It should, however, be noted that the sign of $\Delta E_{yz}$ is likely to depend sensitively on the details of the electronic structure and in particular on the width of the wire. In fact, previous calculations of MAE of free standing wires have already revealed even–odd-like oscillations of the easy axis as a function of the number of Co atoms in the transverse direction [22]. Let us finally remark that large in-plane anisotropies $\Delta E_{xy} = E_x - E_y$ are found on both monatomic and biatomic wires. For example, $\Delta E_{xy} = 0.52, 0.40$ and 0.42 meV for $\text{Co}_3$, $\text{Co}_{10}$ and $\text{Co}_{12}$ on Pd(110), respectively. Therefore, simple uniaxial models of magnetic anisotropy are not strictly applicable in these cases.

The previous discussion shows that the interactions between magnetic ad-atoms and metallic substrates often lead to redistributions of the spin-polarized density and to changes in the electronic structure which have a strong influence on the SO energies. This offers numerous possibilities of tailoring the magneto-anisotropic properties by an appropriate choice of the substrate, the deposited material and their morphology. A first insight into this problem is provided by figure 3 where the MAEs of an infinite 1D chain are reported as a function of wire–substrate distance. This is equivalent to tuning wire–substrate hybridizations in a systematic way and allows us to test the sensitivity of the MAE to small variations of the wire–substrate distance around the equilibrium value. First of all, one observes that reasonable changes of $d_{\text{Co–Pd}}$ around $d_{\text{av}} = \frac{1}{2}[d_{\text{Co–Co}}(\text{bulk}) + d_{\text{Pd–Pd}}(\text{bulk})]$ do not change significantly the quantitative results and, in particular, the stability of the off-plane magnetization direction. For large $d_{\text{Co–Pd}}$ one obtains, as expected, an in-line easy axis as in free-standing chains. On the other hand, for small $d_{\text{Co–Pd}}$ one observes a decrease and change of sign of $\Delta E_{xz}$ due to a reduction of the Co and Pd local moments.
3.3. Local environment effects

The local formulation given in section 2 allows us to express most relevant magnetic properties as a sum of contributions corresponding to the different atoms $i$ of the wire and its surroundings. In this way the observed magnetic behaviour of the deposited chains can be related to the specific local atomic environments. As an example we consider the monatomic $\text{Co}_6$ and the biatomic $\text{Co}_{12}$ chains on Pd(110). In tables 3 and 4 we report the corresponding local spin moments $\langle S_{iz} \rangle$, the local orbital moments $\langle L_{i\delta} \rangle$ for $\delta = x, y$ and $z$ and the total local moments $\mu_i = 2\langle S_{i\delta} \rangle + \langle L_{i0} \rangle$ along the easy axis ($\delta_0 = z$ for the $\text{Co}_6$ chain, and $\delta_0 = y$ for the $\text{Co}_{12}$ bichain). The labelling of the relevant atomic sites $i$ is given in figures 1 and 2. Notice that in the presence of SO interactions the local symmetry operations are reduced to those leaving the magnetization direction unchanged, including the magnetization inversion $\vec{M} \rightarrow -\vec{M}$ due to time-inversion symmetry. Thus, the point-group symmetries are lower for in-plane magnetizations.

The local spin moments $\langle S_{iz} \rangle$ at the Co atoms are nearly saturated and therefore they are quite independent of $i$ and of the monatomic or biatomic type of wire. In contrast, the $\langle S_{iz} \rangle$ induced at the Pd atoms show a very interesting environment dependence. In fact, $\langle S_{iz} \rangle_{\text{Pd}}$ appears to correlate very well with the number of Co atoms $z_i$ that are NNs of the Pd atom $i$, namely, larger $z_i$ corresponds to larger $\langle S_{iz} \rangle$. For example in $\text{Co}_6$ for $i = 7$–10 and $i = 21$–26 we have $z_i = 1$ and $\langle S_{iz} \rangle = 0.18$–0.21 $\mu_B$, while for $i = 11$–20 we have $z_i = 2$ and $\langle S_{iz} \rangle = 0.26$–0.29 $\mu_B$ (see table 3 and figure 1). A similar trend is found in the $\text{Co}_{12}$ bichain. Here, we have $z_i = 1$ and $\langle S_{iz} \rangle = 0.19$–0.25 $\mu_B$ for $i = 13$–16 and 34–45, $z_i = 2$ and $\langle S_{iz} \rangle = 0.20$–0.30 $\mu_B$ for $i = 17$–28 and $z_i = 4$ and $\langle S_{iz} \rangle = 0.35$–0.39 $\mu_B$ for $i = 29$–33 (see table 4 and figure 2). Strong correlations between local magnetic moments and the immediate chemical environment of the atoms have been already observed in small 2D Co islands deposited on Pd(111) and in magnetic

![Figure 3](http://www.njp.org/)
Table 3. Local magnetic properties of a monatomic Co₆ chain deposited on the Pd(110) surface. The spin moments \(2\langle S_{iz}\rangle\), orbital moments \(\langle L_{i\delta}\rangle\) for \(\delta = x, y\) and \(z\) and total magnetic moment \(\mu_{iz} = 2\langle S_{iz}\rangle + \langle L_{iz}\rangle\) along the easy axis \(z\) are given in Bohr magnetons for the different atomic sites \(i\), as labelled in figure 1. The corresponding local magneto-crystalline anisotropy energies \(\Delta E_{xz}(i) = E_x(i) - E_z(i)\), \(\Delta E_{yz}(i) = E_y(i) - E_z(i)\) and \(\Delta E_{xy}(i) = E_x(i) - E_y(i)\) are given in millielectron volts (see equations (8) and (9)). The last line reports the average values per Co atom.

| \(i\) | \(2\langle S_{iz}\rangle\) | \(\langle L_{iz}\rangle\) | \(\langle L_{iy}\rangle\) | \(\langle L_{iz}\rangle\) | \(\mu_{iz}\) | \(\Delta E_{xz}\) | \(\Delta E_{yz}\) | \(\Delta E_{xy}\) |
|------|----------------|----------------|----------------|----------------|-------------|-------------|-------------|-------------|
| 1–2  | 1.62           | 0.33           | 0.33           | 0.29           | 1.91        | 0.96        | -0.83       | 1.79        |
| 3–4  | 1.65           | 0.34           | 0.29           | 0.26           | 1.91        | -0.61       | 0.47        | -1.08       |
| 5–6  | 1.65           | 0.33           | 0.28           | 0.28           | 1.93        | 1.04        | 1.09        | 0.05        |
| 7–10 | 0.18           | 0.03           | 0.03           | 0.04           | 0.22        | 0.28        | 0.24        | 0.04        |
| 11–14| 0.26           | 0.03           | 0.04           | 0.05           | 0.31        | -0.08       | -0.53       | 0.45        |
| 15–18| 0.29           | 0.04           | 0.05           | 0.06           | 0.35        | -0.15       | -0.33       | 0.18        |
| 19–20| 0.29           | 0.04           | 0.05           | 0.06           | 0.35        | -0.35       | -0.71       | 0.36        |
| 21–22| 0.20           | 0.01           | 0.03           | 0.03           | 0.23        | 0.62        | 1.66        | -1.04       |
| 23–24| 0.21           | 0.00           | 0.03           | 0.03           | 0.24        | 1.11        | 1.40        | -0.29       |
| 25–26| 0.21           | 0.00           | 0.03           | 0.03           | 0.24        | 0.94        | 0.45        | 0.49        |
| Av.  | 2.42           | 0.42           | 0.43           | 0.43           | 2.85        | 1.26        | 0.86        | 0.40        |

Alloys which involve, as in the present case, non-saturated magnetic moments (e.g., Fe–Al or Fe–Co alloys) [42]. It should moreover be noticed that for these small chains the number of Pd atoms at the Co–Pd interface is roughly three times the number of Co atoms. Therefore, the induced Pd moments yield a very significant contribution to the average magnetic moment per Co atom (see table 1).

The local orbital moments \(\langle L_{i\delta}\rangle\) at the Co atoms are typically a factor of two to three larger than in bulk Co and show a rather weak dependence on \(i\). This is probably due to the fact that all Co atoms in the chain have a similar local environment (e.g., the same number of Pd NNs). For the Pd atoms at the Co–Pd interface the orbital moments are far less important in absolute values (\(\langle L_{i\delta}\rangle = 0.03–0.06 \, \mu_B\)). However, in most cases they still represent about 10–20% of the total Pd moments \(\mu_{i\delta}\), which is comparable to the 15–20% orbital contribution to \(\mu_{i\delta}\) in the case of Co.

The local anisotropy energies \(\Delta E_{\delta\gamma}(i) = E_\delta(i) - E_\gamma(i)\) are also reported in tables 3 and 4 in order to discuss in particular the microscopic origin of the perpendicular magnetization in 1D Co₆/Pd(110). The Pd atoms close to Co₆ cannot be regarded as a mere source of modifications in the electronic structure of Co₆ 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 SO couplings (\(\xi_{\text{Pd}} \approx 2\xi_{\text{Co}}\)) [39]. Therefore they contribute to \(\Delta E_{xz}\) and to the overall MAE of the system. In fact, \(\Delta E_{xz}(i)\) of Pd atoms is of the same order of magnitude as in Co atoms, often even larger at Pd (see tables 3 and 4). Notice that if one neglected the Pd-atom contributions to the MAE, the value of \(\Delta E_{xz}\) would be greatly underestimated.
Table 4. Local magnetic properties of a biatomic Co$_{12}$ chain deposited on the Pd(110) surface. The spin moments $2\langle S_{iz} \rangle$, orbital moments $\langle L_{i\delta} \rangle$ for $\delta = x$ and $z$ and total magnetic moment $\mu_{iy} = 2\langle S_{iy} \rangle + \langle L_{iy} \rangle$ along the easy axis $y$ are given in Bohr magnetons for the different atomic sites $i$ as labelled in figure 2. The corresponding local magneto-crystalline anisotropy energies $\Delta E_{xz}(i) = E_x(i) - E_z(i)$, $\Delta E_{yz}(i) = E_y(i) - E_z(i)$ and $\Delta E_{xy}(i) = E_x(i) - E_y(i)$ are also shown in millielectron volts (see equations (8) and (9)). The last line reports the average values per Co atom.

| $i$ | $2\langle S_{iz} \rangle$ | $\langle L_{iz} \rangle$ | $\langle L_{iy} \rangle$ | $\langle L_{iz} \rangle$ | $\mu_{iy}$ | $\Delta E_{xz}$ | $\Delta E_{yz}$ | $\Delta E_{xy}$ |
|-----|-----------------|-----------------|-----------------|-----------------|--------|--------------|--------------|--------------|
| 1–4 | 1.62            | 0.32            | 0.31            | 0.27            | 1.93   | 0.13         | 0.01         | 0.12         |
| 5–8 | 1.66            | 0.31            | 0.29            | 0.26            | 1.95   | –0.36        | –0.39        | 0.03         |
| 9–12| 1.66            | 0.31            | 0.27            | 0.28            | 1.93   | 0.68         | 0.25         | 0.43         |
| 13–16| 0.19           | 0.03            | 0.05            | 0.05            | 0.24   | 0.24         | 0.12         | 0.12         |
| 17–20| 0.25           | 0.03            | 0.04            | 0.04            | 0.29   | –0.12        | –0.66        | 0.54         |
| 21–24| 0.30           | 0.04            | 0.05            | 0.06            | 0.35   | –0.42        | –0.10        | –0.32        |
| 25–26| 0.30           | 0.04            | 0.05            | 0.06            | 0.35   | –0.46        | –0.49        | 0.03         |
| 27–28| 0.20           | 0.03            | 0.04            | 0.04            | 0.24   | 0.20         | 0.18         | 0.02         |
| 29–30| 0.35           | 0.04            | 0.04            | 0.05            | 0.39   | –0.70        | –1.67        | 0.97         |
| 31–32| 0.39           | 0.05            | 0.05            | 0.06            | 0.44   | –0.47        | –0.50        | 0.03         |
| 33  | 0.39            | 0.05            | 0.06            | 0.06            | 0.45   | –0.30        | –0.39        | 0.09         |
| 34–37| 0.21           | 0.01            | 0.04            | 0.03            | 0.25   | 0.56         | 0.56         | 0.00         |
| 38–41| 0.24           | 0.01            | 0.04            | 0.03            | 0.28   | 0.32         | 0.37         | –0.05        |
| 42–45| 0.25           | 0.01            | 0.04            | 0.03            | 0.29   | 0.41         | 0.44         | –0.03        |
| Av. | 2.37            | 0.41            | 0.41            | 0.39            | 2.78   | 0.20         | –0.22        | 0.42         |

4. Conclusion

The spin magnetic moments, orbital magnetic moments and MAE of Co$_N$ wires ($N \leq 12$) deposited on the Pd(110) surface have been investigated theoretically in the framework of an SCTB method. A variety of interesting behaviours have been revealed, for example, the contribution of Pd atoms to the magnetization per Co atom, the enhancement of orbital magnetism and of the MAE in deposited Co wires and the possibility of stable wire magnetization perpendicular to the Pd surface. The importance of the substrate contributions to the magnetoanisotropic behaviour of TM wires deposited on highly polarizable metallic substrates has been demonstrated. Besides the interest in these specific systems, the present study should encourage the development of new experimental works as well as further theoretical improvements.

Acknowledgments

This work has been supported by EU GROWTH project AMMARE (contract number G5RD-CT-2001-00478), by CONACyT of Mexico (grant numbers 32085E and W-8001-millenium) and by IMP of Mexico (grant number FIES-98-101-I). Computer resources were provided by IDRIS (CNRS, France).
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