Anomalous ferromagnetism of a monatomic Co wire at the Pt(111) surface step edge

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A first-principles investigation of the anomalous ferromagnetism of a quasi-one-dimensional Co chain at the Pt(111) step edge is reported. Our calculations show that the symmetry breaking at the step leads to an easy magnetization axis at an odd angle of ~20° *towards* the Pt step, in agreement with experiment [P. Gambardella *et al.*, Nature (London) **416**, 301 (2002)]. Also, the Co spin and orbital moments become noncollinear, even in the case of a collinear ferromagnetic spin arrangement. A significant enhancement of the Co orbital magnetic moment is achieved when modest electron correlations are treated within LSDA+*U* calculations.

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Exploring magnetism in the one-dimensional (1D) limit has been a great challenge for many years. Only recently, Gambardella *et al.*[1] succeeded to observe ferromagnetism of monatomic Co wires decorating the Pt(997) surface step edge. By exploiting the element-selectivity of the x-ray magnetic circular dichroism (XMCD), the existence of long-range-like ferromagnetic order on Co was demonstrated below 15 K.[1,2] Although theoretically the Mermin-Wagner theorem[3] forbids long-range 1D ferromagnetic order at nonzero temperatures, ferromagnetism in 1D can be stabilized by a large magnetic anisotropy energy, which creates barriers effectively blocking thermal fluctuations. The significance of such a blocking mechanism was recognized earlier for the occurrence of long-range magnetic order in 2D systems.[4,5]

The experiments of Gambardella *et al.* revealed novel magnetic properties of monatomic Co wires at Pt step edges. An unexpected magnetocrystalline anisotropy was observed: the easy magnetization axis was directed along a peculiar angle of +43° towards the Pt step edge and normal to the Co chain. The magnetocrystalline anisotropy energy (MAE) was estimated to be substantial, of the order of 2 meV/Co atom.[1] In addition, a considerable enhancement of the Co orbital magnetic moment $M_L \approx 0.7\mu_B$—as compared to the bulk Co M_L value of $0.14\mu_B$—was deduced from XMCD experiments.

In this paper we report a first-principles investigation of the anomalous ferromagnetism of a monatomic Co wire at the Pt(111) surface step edge, using state-of-the-art electronic structure calculations. We focus on the intriguing features of the quasi-1D Co wire: i.e., the easy axis rotated away from the (111) surface normal, the enhanced Co orbital moment, and the huge estimated MAE. The key outcomes of our study are (i) the *ab initio* calculation of an easy axis at an odd angle rotated towards the Pt step edge and (ii) the prediction of an intrinsic noncollinearity between spin and orbital magnetic moments of both the ferromagnetic, Co wire and Pt substrate. The origin of this novel magnetic behavior, which is to our knowledge not present in known 2D and 3D itinerant ferromagnets is explained to be a consequence of the magnetic symmetry lowering at the surface step edge.[6] Our calculations furthermore yield a MAE of the order of 4 meV/Co atom and—using the LSDA+*U* approach—a Co orbital moment $M_L = 0.45\mu_B$.

Previously, several computational studies of the magnetic properties of adatoms, clusters, and monatomic chains on surfaces were reported (see, e.g., Refs. 7–11). The calculations predict in general an enhanced MAE closely related to the reduced dimensionality. However, in all of these studies only transition-metal wires or adatoms on *flat* surfaces are investigated—i.e., geometries that are essentially different from the metal wire at a step edge. For wires, adatoms or clusters[8] at flat surfaces the easy axis is either normal to the surface or in-line for some wires.[11] So far only one *ab initio* study of Co at a Pt step edge was reported, in which the XMCD spectrum was computed,[12] but the magnetic anisotropy was not considered. Our study focuses on the unprecedented magnetic anisotropy properties observed for the quasi-1D Co chain.

Methodology. We performed supercell calculations to model the Co chain at the Pt(111) surface step edge. Supercells of various sizes were investigated. We shall discuss here particularly two supercells: one of small size, model I, and a large, realistic supercell, model II (see Fig. 1). Thus, we can follow the successive changes while approaching the real situation. Model I consists of one subsurface Pt layer built of four rows of Pt atoms and one surface layer containing one row of Co atoms and two rows of Pt atoms, as well as one empty row, to model the step edge. Model II consists of a sub-subsurface and a subsurface Pt layer built of six rows of Pt atoms, while the surface step is modeled by three rows of Pt atoms, one Co row, and two rows of empty Pt sites. In both supercells the vacuum is modeled by the equivalent of two empty Pt layers. All interatomic distances are adopted to be those of pure Pt. We note that while model II reaches the maximally treatable supercell size for full-potential, relativistic calculations of the MAE, the proportions of the experimental Co chain at the Pt(997) step edge are still larger, consisting of an eigtht-Pt-row-wide terrace at the Pt step.[2]

The first-principles calculations were performed using the relativistic full-potential linearized-augmented-plane-wave (FP-LAPW) method, in which the spin-orbit coupling (SOC) is included in a self-consistent second-variational

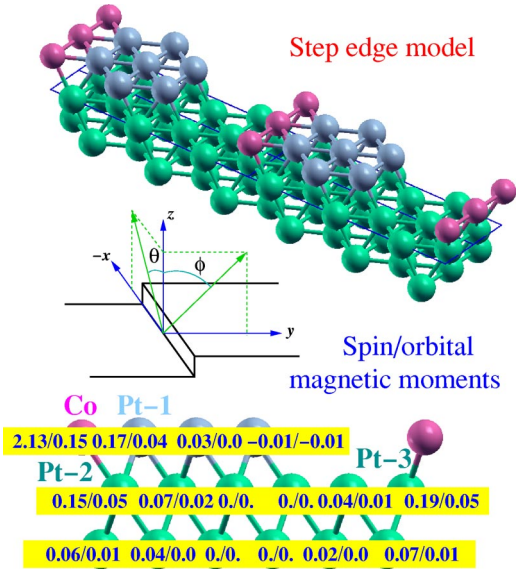

FIG. 1. (Color online) Top: schematic crystal structure of model II, used to represent the Co chain at the Pt(111) surface step edge (Ref. 13). Middle: definition of the angles θ, ϕ, and coordinate axes. The x axis is chosen parallel to $[1\bar{1}0]$ (along the Co wire), the y axis to $[1\bar{2}1]$ (normal to the wire), and the surface normal z is chosen parallel to [111]. Bottom: profile sketch with calculated M_S^z/M_L^z values specified.

procedure.[14] For most of the calculations the conventional (von Barth-Hedin) local spin-density approximation (LSDA) is adopted, which is expected to be valid for itinerant metallic systems. In order to capture better the electron correlations expected for the Co $3d$ electrons in the reduced dimension also the LSDA+U approach, in the implementation of Ref. 15, has been applied. For further details of the calculations, see Ref. 16.

First-principles results. We first applied the conventional LSDA approach using the FP-LAPW scheme. To start with, the spin magnetization axis was chosen to be fixed along either the x, y, or z axis. The essential computed spin ($\vec{M}_S$) and orbital ($\vec{M}_L$) moments are given in Table I. Table I reveals that the $\vec{M}_S$ and $\vec{M}_L$ on Co and Pt are *noncollinear* for a spin moment fixed along the y or z axis, but *collinear* when $\vec{M}_S$ is along the x axis. Noncollinearity of $\vec{M}_S$ and $\vec{M}_L$ has been predicted previously[17] for noncollinear spin magnetic structures, and not for a collinear, ferromagnetic spin configuration. To understand the noncollinearity of $\vec{M}_S$ and $\vec{M}_L$ it is instructive to consider the magnetic symmetry. The symmetry operations which preserve the crystal symmetry are the identity E and the mirror operation σ_x with respect to the yz plane (see Fig. 1). Considering now the magnetic symmetry operations, which are—for a total magnetic moment in the yz plane—E and $\sigma_x R$, with R the time inversion, we observe that these symmetry conditions impose $M^x=0$, but M^y, $M^z\neq 0$ without any restriction. Therefore there is no particular symmetry imposed direction in the yz plane which would force the spin and orbital moment to be parallel. In other words, the magnetic symmetry in the yz plane is the same for all magnetization directions. Along the wire the situation is different: the magnetic symmetry operations E and σ_x, which conserve M^x, force $M^y=M^z=0$ and, consequently, we must have $\vec{M}_L\|\vec{M}_S$ for a magnetization along the wire.

TABLE I. Spin and orbital magnetic moments in μ_B, calculated for the monatomic Co wire at the Pt(111) step edge, using the supercell models I and II.

	$\vec{M}_S$			$\vec{M}_L$		
	x	y	z	x	y	z
Model I, axis						
$\vec{M}_S\|x$ axis	2.129	0	0	0.084	0	0
$\vec{M}_S\|y$ axis	0	2.128	0	0	0.065	0.032
$\vec{M}_S\|z$ axis	0	0	2.127	0	0.009	0.155
Model II, atom[a]						
Co	0	0	2.127	0	0.011	0.149
Pt-1	0	0	0.168	0	0.005	0.044
Pt-2	0	0	0.146	0	0.003	0.046
Pt-3	0	0	0.194	0	0.005	0.052

[a]M_S parallel to the z axis.

From Table I we further observe that both the Co spin and orbital moment are considerably enhanced with respect to the values for bulk hcp Co,[18] as expected for a dimensionality reduction leading to a more atomiclike configuration. The calculated M_S and M_L of Co agree well with those of Ref. 12, where, however, only z-axis collinear components of M_S and M_L were considered. The Co M_S does not change when the supercell is enlarged from model I to model II, but small changes in the orbital moments exist. Also, there is a sizable magnetization induced on the nearest-neighbor Pt atoms, which is decreasing rapidly for the Pt atoms farther away (see Fig. 1). The size of supercell model II appears thus sufficient to separate the magnetic Co wires and to ensure the Pt magnetization decreases away from the step edge.

Next, we turn to the salient aspect of our investigation, the MAE calculations. We used the so-called "magnetic force theorem" to compute the MAE: starting from self-consistent charge and spin densities calculated for the spin moment aligned along the z axis, the M_S is rotated over angles θ or ϕ (see Fig. 1) and a single energy band calculation is performed for the new orientation of M_S. The MAE, which is defined as a directional total-energy difference, is computed from the change in one-electron energies E due to the M_S rotation—i.e., $\mathrm{MAE}=E(\theta,\phi)-E(\theta=0,\phi=0)$ (Ref. 19). The calculated angular dependent MAE is shown in Fig. 2 for supercell II.

For a rotation of M_S over an angle θ in the xz plane the MAE dependence on θ is symmetric, reflecting the mirror symmetry σ_x, with the easier axis pointing along the z direction and the harder axis along the Co wire. For a rotation of M_S over an angle ϕ in the yz plane, we obtain a peculiar asymmetric dependence of the MAE on ϕ, reflecting the absence of any particular symmetry-imposed direction in the yz plane. The computed easy axis is rotated away from the z

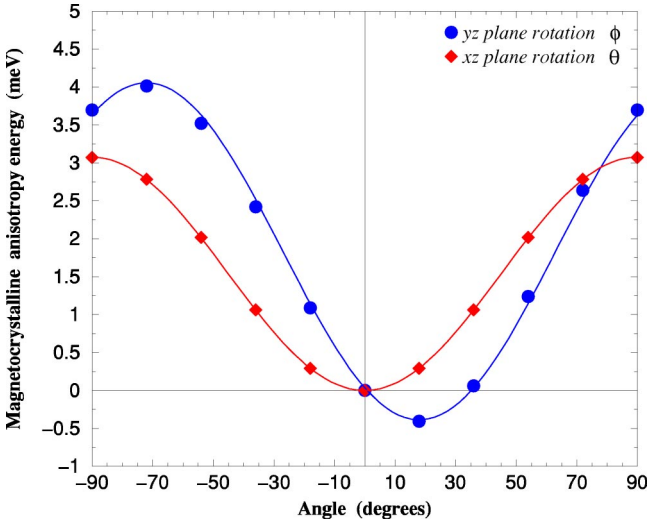

FIG. 2. (Color online) The MAE calculated for model II as a function of the angles θ and ϕ of the spin moment. The solid lines are fits to the points and are given by MAE$=4.04-4.44\cos^2(\phi-18°)$ in the *yz* plane and $3.08-3.08\cos^2\theta$ in the *xz* plane.

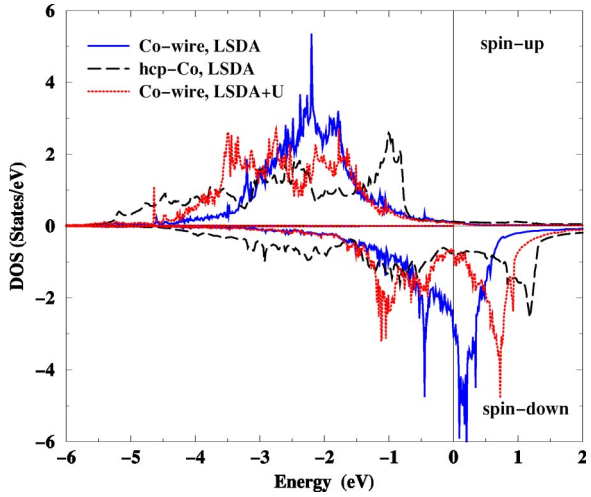

FIG. 3. (Color online) The spin-resolved 3*d* DOS, computed with the LSDA and LSDA$+U$ methods, for model II and compared to the LSDA DOS of hcp bulk Co.

axis by 18° *towards* the Pt step edge, in semiquantitative agreement with the experimentally observed anomalous 43° easy axis.[1] The calculated direction of the hard axis of −72° corresponds reasonably to the experimental value of ≈−50° also. MAE calculations adopting model I lead to similar MAE(θ,ϕ) curves (not shown), yet the minimum occurs for $\phi\approx-50°$— i.e., an outward pointing easy axis. Thus, while both models provide nearly identical moments, increasing the supercell size from model I to II improves the MAE and thus an even better agreement with experiment can be expected for larger supercells. The MAE difference between the hard and easy axes is ≈4.45 meV/Co for model II (≈1.6 meV/Co for model I), which exceeds by an order of magnitude the dipolar shape anisotropy.[20] The MAE is of the same magnitude as the experimentally estimated MAE of ∼2 meV/Co at $T=45$ K.[1] We expect a definitely higher experimental MAE and thus an even better agreement with model II for $T=0$ K. We note that previous studies showed the conventional LSDA theory to be quite successful for describing the uniaxial MAE of hcp Co and CoPt bulk alloy.[21,22] Here we observe that the LSDA also provides a reasonable explanation of the MAE of the Co wire at the Pt step edge.

The source of the large MAE of Co-Pt systems is well understood:[22] the Pt atoms contribute substantially to the MAE through their strong SOC, which couples to the 3*d*-5*d* hybridization-induced Pt exchange splitting. For the Co wire on Pt, the particular shape of the MAE can be further unfolded. We note first that the asymmetric MAE in the *yz* plane can be well fitted by a $\cos^2$ angular dependence, suggesting a uniaxial origin.[6] Adopting a symmetry-based "atomic pair" model[23] the lowest second-order MAE can be written as a sum over Co-atom nearest-neighbor pairs $P(\vec{m}\cdot\vec{R})$, where $\vec{m}$ is the magnetization unit vector, $\vec{R}$ the Co-Pt nearest-neighbor vector, and P an empirical Néel parameter. The MAE then reads $[7/6P_{\text{Co-Pt}_2}+1/3P_{\text{Co-Pt}_3}-3/2P_{\text{Co-Pt}_1}]\cos^2(\phi)+2/3\sqrt{2}[P_{\text{Co-Pt}_2}-P_{\text{Co-Pt}_3}]\sin(\phi)\cos(\phi)$.

Our computed $\cos^2(\phi-\phi_0)$ dependence with $\phi_0\neq0$ occurs only when $P_{\text{Co-Pt}_2}\neq P_{\text{Co-Pt}_3}$ even for $|R_{\text{Co-Pt}_2}|=|R_{\text{Co-Pt}_3}|$. Indeed, at the step edge the Pt-2 and Pt-3 become nonequivalent (see Fig. 1). Their 5*d*-3*d* hybridization is therefore different, which causes the inequality leading to the asymmetric MAE shape.

Although the LSDA works well for MAE calculations, it is known not to give large enough values for the orbital moment.[18] This is in itself unsurprising, as the MAE is not related to the size of M_L but to its anisotropy. The LSDA-calculated M_L of hcp Co is, for example, with $0.08\mu_B$ only half the experimental value of $0.14\mu_B$. The situation is even worse for the Co wire. Comparing the LSDA calculated $M_L\sim0.15\mu_B$ (see Table I) with the experimental M_L of $0.68\pm0.05\mu_B$ (Ref. 1) indicates that the LSDA value is too small by a factor of 4.5. Recently, the orbital-polarization correction (LSDA+OP) was applied to a Co wire on Pt, leading to a Co M_L of $0.92\mu_B$ (Ref. 12), but this value overshoots the experimental data.

To improve the M_L one needs to account for electron-correlation effects beyond the conventional LSDA, which is currently a challenging problem of *ab initio* relativistic energy-band theory. To estimate this effect, we use here the *semimodel* but physically transparent LSDA$+U$ method, which was shown to correct the Co M_L of both hcp Co and CoPt alloy with a *single* choice of the Coulomb U(=1.7 eV) and exchange J(=0.91 eV) parameters.[21] Using the same U and J, we compute $M_L^z=0.45\mu_B$ when M_S is along the *z* axis, still smaller than the experiment. The Co spin moment hardly changes, from $2.13\mu_B$ to $2.18\mu_B$ when the U is included. We could of course obtain better agreement with experiment by another choice of U and J, but we prefer to use the "universal" values found in Ref. 21, treating thus the U of metallic Co as a transferable, atom-specific quantity.

This value of U is supported also by the Co wire 3*d* density of states (DOS) shown in Fig. 3. Since the LSDA DOS shows a clear metallic behavior, there is no reason to

expect a significant change in screening as compared to elemental Co. The spin-resolved LSDA DOS reveals a substantial narrowing of the bandwidth from ~6 eV for hcp Co to ~4 eV for the Co wire as well as a moderate increase of the spin splitting, as is expected for the reduced Co coordination. When the U is included, the 3d DOS broadens somewhat and significant changes in the spin-resolved DOS occur due to the enhanced orbital polarization. The M_L enhancement is found to be brought about by modifications of the in-plane spin-down x^2-y^2 and xy orbital densities which are affected most by the missing Pt atoms at one edge side and thus most liable to locaize. In the LSDA+U approach the MAE can be computed rigorously only from total energies,[15,21,24] as it is incompatible with the force theorem. Leaving these calculations for the future, we recall again that the Coulomb-U-induced increase of M_L does not necessarily imply a corresponding change in the MAE.

In conclusion, employing first-principles calculations we have provided a microscopic picture of the anomalous magnetocrystalline anisotropy of a quasi-1D Co chain at the Pt(111) step edge. The essential symmetry breaking at the step edge leads to noncollinear spin and orbital moments as well as to an easy magnetization axis oriented at a peculiar angle towards the Pt step edge. LSDA theory is found to provide a rather good explanation of the magnetocrystalline anisotropy, yet a considerable improvement of the Co orbital moment is obtained with LSDA+U calculations.

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