Anomalous Ferromagnetism of Monatomic Co Wire at the Pt(111) Surface Step Edge

Alexander B. Shick,1 František Máca,1 and Peter M. Oppeneer2
1Institute of Physics, ASCR, Na Slovance 2, CZ-182 21 Prague 8, Czech Republic
2Leibniz-Institute of Solid State and Materials Research, P.O. Box 270016, D-01171 Dresden, Germany
(Dated: March 22, 2022)

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 \(\sim 20^\circ\) towards the Pt step, in agreement with experiment [P. Gambardella et al., Nature 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.

PACS numbers: 75.30.Gw, 75.75.+a, 75.10.Lp

Exploring magnetism in the one-dimensional (1D) limit has been a great challenge for many years. Only recently, Gambardella et al. succeeded in observing 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 ferromagnetic order on Co was demonstrated below 15 K [1,2]. Although theoretically the Mermin-Wagner theorem forbids long-range 1D ferromagnetic order at non-zero temperatures, ferromagnetism in 1D can be stabilized by a large magnetic anisotropy energy, which creates barriers effectively blocking thermal fluctuations. The significance of such blocking mechanism was recognized earlier for the occurrence of long-range magnetic order in 2D systems [3].

The experiments of Gambardella et al. revealed novel magnetic properties of monatomic Co wires at Pt step edges. An unexpected magneto-crystalline anisotropy was observed: the easy magnetization axis was directed along a peculiar angle of \(+43^\circ\) towards the Pt step edge and normal to the Co chain. The magneto-crystalline 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 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 breaking at the surface step edge [4]. 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., [5,6,7,10,11]). The calculations predict in general an enhanced MAE closely related to the reduced dimensionality and enhancement of the orbital moment. 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 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, a toy model, which we name model I, and a large, realistic supercell, model II (see Fig. 1). Model I consists of one subsurface Pt layer built of 4 rows of Pt and one surface layer containing one row of Co atoms, two rows of Pt, 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 6 rows of Pt atoms, while the surface step is modeled by 3 rows of Pt, 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 approaches the maximally treatable supercell size for full-potential, relativistic calculations of the MAE, the proportions of the experimental Co chain...
FIG. 1: Top: schematic crystal structure of model II, used to represent the Co chain at the Pt(111) surface step edge. Middle: Definition of the angles \( \theta, \phi \), and coordinate axes. The \( x \) axis is chosen parallel to [110] (along the Co wire), the \( y \) axis to [121] (normal to the wire), and the surface normal \( z \) is chosen parallel to [111]. Bottom: profile sketch with calculated \( M_z \) values specified.

at the Pt(997) step edge are still larger, consisting of an 8 Pt rows wide terrace at the Pt step.

The first-principles calculations were performed using the relativistic full-potential linearized-augmented-plane-wave (FP-LAPW) method, in which the spin-orbit coupling is included in a self-consistent second-variational procedure. 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. has been applied. For further details of the calculations, see Ref.

First-principles results. We first applied the conventional LSDA approach using the FP-LAPW method. To start with, the spin magnetization axis was chosen to be fixed either along the \( x, y \), or \( z \) axis. The essential computed spin \( \langle \vec{M}_S \rangle \) and orbital \( \langle \vec{M}_L \rangle \) 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 for materials exhibiting a noncollinear spin magnetic structure, but this is to our knowledge the first observation of such noncollinearity 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 \( \sigma_x \) 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 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 \( \sigma_x \), which conserve \( M_x \), force \( M_y = M_z = 0 \) and consequently, we must have \( \vec{M}_L \parallel \vec{M}_S \) for a magnetization along the wire.

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, as expected for a dimensionality reduction leading to a more atomic-like configuration. The calculated \( M_S \) and \( M_L \) of Co agree well with those of Ref. 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 decrease 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

| Model I, axis | \( x \) | \( y \) | \( z \) | \( x \) | \( y \) | \( z \) |
|---------|------|------|------|------|------|------|
| \( \vec{M}_S \parallel x \) axis | 2.129 | 0 | 0 | 0.084 | 0 | 0 |
| \( \vec{M}_S \parallel y \) axis | 0 | 2.128 | 0 | 0 | 0.065 | 0.032 |
| \( \vec{M}_S \parallel z \) axis | 0 | 0 | 2.127 | 0 | 0.009 | 0.155 |

| Model II, atom | \( M_x \) | \( M_y \) | \( M_z \) |
|---------|------|------|------|
| Co | 0 | 0 | 2.127 |
| Pt-1 | 0 | 0 | 0.168 |
| Pt-2 | 0 | 0 | 0.146 |
| Pt-3 | 0 | 0 | 0.194 |

\( \vec{M}_S \) parallel \( z \) axis
spin moment aligned along the z axis, the $M_S$ is rotated over angles $\theta$ or $\phi$ (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., MAE = $E(\theta, \phi) - E(\theta = 0, \phi = 0)$. The calculated MAE is shown in Fig. 2 for supercell II.

For a rotation of $M_S$ over an angle $\theta$ in the $xz$ plane the MAE dependence on $\theta$ is symmetric, reflecting the mirror symmetry $\sigma_z$, with the easy axis pointing along the $z$ direction and the hard axis directed along the Co wire. A MAE difference between the hard and easy axes of $\sim 3$ meV/Co ($\sim 1$ meV/Co for model I) is calculated, exceeding by an order of magnitude the dipolar shape anisotropy.

For a rotation of $M_S$ over an angle $\phi$ in the $yz$ plane, we obtain a peculiar asymmetric dependence of the MAE on $\phi$ (see Fig. 2), reflecting the absence of any particular symmetry imposed direction in the $yz$ plane. The computed easy axis is rotated away from the $z$ axis by $18^\circ$ towards the Pt step edge, in semi-quantitative agreement with the experimentally observed anomalous $43^\circ$ easy axis. The calculated direction of the hard axis of $-72^\circ$ corresponds reasonably with the experimental value of $\approx -50^\circ$ also. A notable difference appears for MAE calculations adopting model I: while the calculated MAE($\phi = 0$) curve is asymmetric as well, the minimum occurs at $\approx -50^\circ$ (not shown), thus oriented outwards from the Pt step. In contrast to supercell model II the toy model I is not even qualitatively for the MAE. Increasing the supercell size from model I to II improves the MAE, therefore an even better agreement with experiment can be expected for even larger supercells. The MAE difference between the hard and easy axes is $\approx 4.45$ meV/Co for model II ($\approx 1.6$ meV/Co for model I), which is of the same magnitude as the experimentally estimated MAE of $\sim 2$ meV/Co at $T = 45$ K. 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.

Although the LSDA works well for MAE calculations, it does not give large enough values for the orbital moment. For example, the LSDA calculated $M_L$ of hcp Co is 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 $M_L$ $\sim 0.15$ $\mu_B$ (see Table I) with the experimental $M_L$ of 0.68 $\pm 0.05$ $\mu_B$ 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 $\mu_B$, 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 semi-model 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. Using the same $U$ and $J$, we compute $M_L^I = 0.45 \mu_B$ for supercell II when $M_S$ is along the $z$ axis ($M_L^I = 0.32 \mu_B$ for model I). These values are still smaller than the experiment but we expect a larger $M_L$ with a further increase of the supercell, due to a related Co $d$-states localization. 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. The Co spin moment hardly changes, from 2.13 to 2.18 $\mu_B$ when the $U$ is included. We note, that in the LSDA+$U$ method the MAE can be computed only from total energies, as it is incompatible with the force theorem. It will require highly accurate self-consistent calculations for the $M_S$ rotated over different angle $\theta$ and $\phi$, something which is numerically not a practicable approach.

To understand how the enlargement of the Co $M_L$ in the LSDA+$U$ approach comes about we consider the spin and orbitally resolved $3d$ densities of states (DOS) of model II, which are shown in Fig. 3. The spin-resolved LSDA DOS reveals a substantial narrowing of the band width from $\sim 6$ eV for hcp Co to $\sim 4$ eV for the Co wire as well as a moderate increase of the spin-splitting (Fig. 3a), as is expected for the reduced Co coordination. When the $U$ is included the $3d$ DOS broadens somewhat and sig-
significant changes in the spin-resolved DOS occur. Since the spin-up Co d-band is fully occupied, only changes of the spin-down band are essential for the $M_L$ enhancement. The spin-down $m$-resolved 3d DOS of the Co wire is shown in Fig. 3b. A major change in the LSDA+$U$ DOS appears as an upward shift within $|\downarrow; m=0\rangle$ DOS, which, however, does not contribute to $M_L$. The major contribution to the increase of $M_L$ originates from an upward shift within $|\downarrow; m=-2\rangle$ and a downward shift of $|\downarrow; m=+2\rangle$ DOS. Also, downward shifts of $|\downarrow; m=\pm 1\rangle$ states take place, but these contribute only secondarily to the $M_L$ change. Thus, we conclude that the $M_L$ enhancement with the Coulomb $U$ is brought about by modifications of the in-plane spin-down $x^2-y^2$ and $xy$ orbital densities and much less affected by changes in the out-of-plane $xz, yz$, and $3z^2-r^2$ orbital densities. The in-plane orbitals are affected most by the missing Pt atoms at one edge side and thus most liable to localize.

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 consider-

able improvement of the Co orbital moment is obtained with LSDA+$U$ calculations.

We gratefully acknowledge discussions with P. Gambardella, P. Novák, H. Eschrig, and W.E. Pickett. This work was supported by the State of Saxony and the Grant Agency of the ASCR Grant A1010214.

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