Giant Magnetocrystalline Anisotropies of 4*d* Transition-Metal Monowires

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The magnetocrystalline anisotropy energy (MAE) for ferromagnetic and antiferromagnetic freestanding monowires of 4*d* transition metals is investigated on the basis of first-principles calculations. Across the 4*d* series, the easy axis of the magnetization oscillates between two directions: perpendicular and along the wire axis. The largest values of the MAE occur at the end of the series. Giant values of 30–60 meV/atom can be obtained upon stretching Ru or Rh wires. Ru and Pd chains change the magnetization direction upon wire stretching, opening new perspectives in controlling the spin-dependent ballistic conductance in these structures.

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Novel experiments [1–4] on one-dimensional (1D) magnetic systems opened a new vista in nanomagnetism and nanospintronics. They stimulated extensive theoretical investigations [5–12] which predicted a wide spectrum of magnetic phenomena and properties unknown in higher dimensions. Particularly fascinating are the perspectives of these 1D systems for spin-dependent quantum transport properties, ballistic anomalous magnetoresistance [13], spin and magnetization tunneling [14], and the presence of Glauber dynamics [15]. It is important to notice that all these properties hinge directly on one quantity: the magnetic anisotropy. More accurately, it is the magnetocrystalline anisotropy energy (MAE), arising predominantly from spin-orbit interaction (SO). It is surprising how little attention has been paid so far to this most relevant quantity, although in bulk and film magnetism the nature of the MAE is a key issue [16]. While monoatomic 3*d*, 4*d*, and 5*d* transition-metal chains are under intensive experimental and theoretical investigation, the MAE has been investigated practically only for Co and Fe. First tight-binding model calculations of the MAE were reported for bare Co and Fe chains and a Co chain deposited on a Pd surface [9]. *Ab initio* values of the MAE and orbital magnetic moments have been reported so far for freestanding chains of Fe [17], Co [18], and a Co chain deposited on Pt [2,19,20].

Considering the utmost importance of the anisotropy as an energy barrier determining the magnetic stability, transport, and dynamical properties of 1D systems, in this Letter we investigate the chemical trend of the MAE and the spin (μ_S) and orbital (μ_L) magnetic moment across the transition-metal series with the aim of unraveling the underlying laws determining, modifying, and controlling these properties. We are aiming at 1D systems with large MAEs and study therefore 4*d* and (partly) 5*d* metallic monowires (MWs), elements which are nonmagnetic as bulk or film systems. Although here we study freestanding transition-metal MWs, the underlying chemical trends hold also for chains deposited on weakly interacting substrates [21] or wires encapsulated inside 1D tubular structures [17], but the actual values of the MAE might be smaller. Throughout this Letter we define MAE as the total-energy difference between two extremal magnetization directions: the axial direction along the wire axis ($\mathbf{z}$) and the one orthogonal to it ($\mathbf{r}$).

We found that the MAE of the 4*d* wires is 1 order of magnitude larger than those of the 3*d* transition-metal films [16]. This fact can be attributed not only to the larger spin-orbit coupling constant, but also to the reduced coordination in these systems, responsible for the lack of quenching of the spin and orbital moments. Giant values of the MAE on the order of 30–60 meV/atom are obtained upon stretching of Ru and Rh monowires. Moreover, we predict that for Ru and Pd MWs their easy magnetization axes change at certain interatomic distances, opening new interesting perspectives in controlling the spin-dependent ballistic magnetoresistance [13] in these systems.

The *ab initio* calculations were carried out in the generalized gradient approximation [22] to the density functional theory, employing the full-potential linearized augmented plane-wave method for 1D systems [17], as implemented in the FLEUR code [23]. For calculations of equilibrium interatomic distances and magnetic ground-state electronic properties without SO we included basis functions with plane waves up to $k_{\max} = 4.0\ \text{a.u.}^{-1}$ and used 32 k points in one half of the 1D Brillouin zone. Spin-orbit coupling was included self-consistently in a nonperturbative manner [24]. Reliable values of the magnetic anisotropy energy have been obtained with $k_{\max}$ of $4.4\ \text{a.u.}^{-1}$ and 300 k points (equivalent to 108×10^6 k points in 3D). The small magnetostatic contribution to the MAE of about 0.1 meV/atom was neglected.

The magnetic properties of 4*d* transition-metal MWs at the equilibrium interatomic distance d_0 are summarized in Fig. 1. We found ferromagnetic (FM) ground-states for Zr, Ru, Rh and Pd, and antiferromagnetic (AFM) ones for Mo and Tc. Y and Nb wires, being borderline cases, are nonmagnetic (NM). This is in agreement with the results of Spišák and Hafner [8]. Characteristic for 1D systems is the

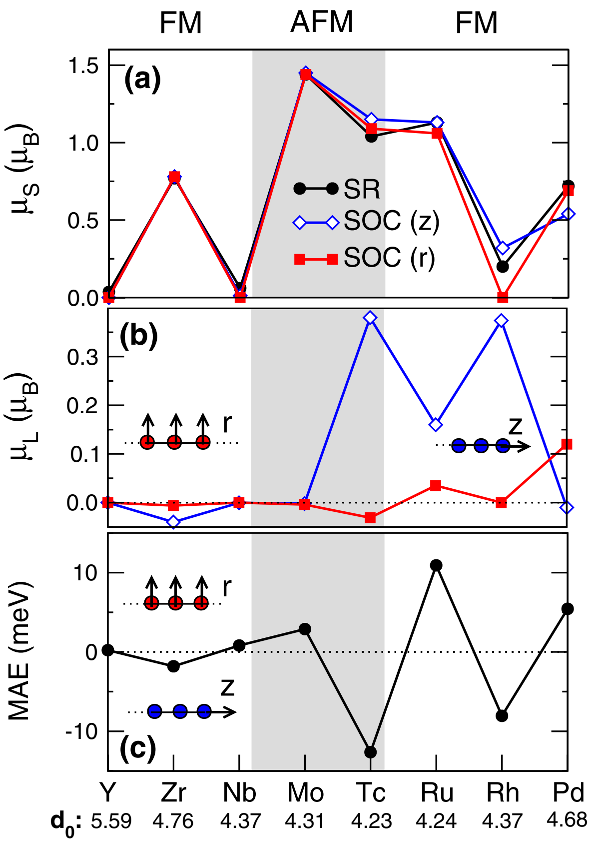

FIG. 1 (color online). Magnetism in 4*d* transition-metal monowires at the equilibrium interatomic distance d_0: (a) total (for elements with FM ground states) and muffin-tin (for AFM ground states) magnetic moment without and with SO (for both magnetization directions), (b) orbital magnetic moments for both magnetization directions, (c) magnetocrystalline anisotropy energy. SR stands for calculations without SO. The equilibrium (SR) interatomic distances d_0 are given in atomic units.

reduced hopping of electrons due to the lack of neighboring atoms in two dimensions. This results in a reduction of the kinetic energy and consequently to a band narrowing and a large density of states (DOS). Compared to three- and two-dimensional systems, in 1D systems the competition between kinetic energy and exchange gives weight to exchange and thus many 4*d* MWs are magnetic although they are nonmagnetic as bulk systems. This is consistent with the Stoner model, which explains the origin of the magnetism on basis of a large NM DOS $n(E_F)$ at the Fermi energy (E_F). Most 4*d* MWs fulfill the Stoner criterion, $In(E_F) > 1$, if I is the intra-atomic exchange parameter. Modulations of the DOS due to the band topology, the formation of van Hove singularities and the position of E_F depending on the band filling are then responsible for a particular NM, FM, or AFM ground state of the wires. The largest values of the magnetization energy, defined as a total-energy difference between the NM and the ground-state magnetic solution, are observed for the AFM Mo and Tc MWs (197 and 53 meV, respectively). The influence of SO on the magnetization energy amounts to less than a few meVs. Significant SO-induced changes in the values of μ_S can be seen especially in the right half of the 4*d* row [Fig. 1(a)]. This leads, in particular, to a zero spin moment in a Rh MW, when the spin-quantization axis, or, equivalently, the magnetization, is chosen to be perpendicular to the chain axis.

Including SO results in a removal of band degeneracies and orbital moments arise [25] [see Fig. 1(b)]. For the early 4*d* metals, left part of the 4*d* row, the values of μ_L are rather small since most occupied bands are involved in chemical bonding. At the same time, Tc, Ru, and Rh MWs exhibit values of 0.2–0.4μ_B. This is in the range of 0.2–0.3μ_B obtained for an Fe MW [17]. For the latter chains we observed a strong dependence of the orbital moment on the magnetization direction. Typically, the axial magnetization leads to values $\mu_L(\mathbf{z})$ that are significantly larger than those for the radial magnetization, $\mu_L(\mathbf{r})$.

The MAE [Fig. 1(c)] as a function of the nuclear number or of the band filling follows roughly the same trend as the orbital moment $\mu_L(\mathbf{z})$. The argument that the energy induced by SO can be assumed to be proportional to the projection of the spin on the orbital momentum $-\mathbf{S}\cdot\mathbf{L}$, leading to an easy magnetization axis in the direction of maximum orbital moment, is hardly applicable anymore for heavier 4*d* transition-metal chains. Here, the SO becomes stronger and the exchange splitting smaller than in 3*d* metals. Nevertheless, we observe that in the case when $\mu_L(\mathbf{z}) \gg \mu_L(\mathbf{r})$, the easy magnetization axis always points along the chain. On the other hand, whenever the difference $|\mu_L(\mathbf{z}) - \mu_L(\mathbf{r})|$ approaches 0.1μ_B, no predictions on the preferred magnetization direction can be made *a priori*. The calculated values of the MAE at the equilibrium interatomic distance d_0 are in the range of 6–12 meV/atom. The values are larger than those for the 3*d* transition-metal chains in a wide range of the interatomic distance [2,17], a consequence of the much larger SO strength of 4*d* metals as compared to the 3*d* ones.

In order to investigate the origin of the orbital magnetism and the oscillatory behavior of μ_L as a function of the band filling, we analyze the band structures of Ru and Rh chains at the interatomic distance of 4.8 a.u. (Fig. 2), a distance offering large exchange and spin-orbit splittings for both magnetization directions. Ignoring the SO, according to the symmetry of a monowire, the *s* and *d* electron wave functions of the metal are grouped into three sets of bands: the two singly degenerate bands $\Delta_1(s, d_{z^2})$, the doubly degenerate $\Delta_3(d_{xz}, d_{yz})$ and $\Delta_4(d_{x^2-y^2}, d_{xy})$ bands. The Δ_4 bands are quite narrow since they originate from wave functions which have nodes from atom to atom along the chain, while Δ_3 bands are more dispersive due to overlapping orbitals along the *z* axis [12]. Each of these bands is exchange split into majority and minority bands. The value of this splitting correlates with the magnetic moment of the system ($\mu_S^{\mathrm{Ru}} = 2.00\mu_B$, $\mu_S^{\mathrm{Rh}} = 0.80\mu_B$) and the band character. The largest splitting of about 0.75 eV/μ_B is found for the slowly dispersing Δ_4 bands.

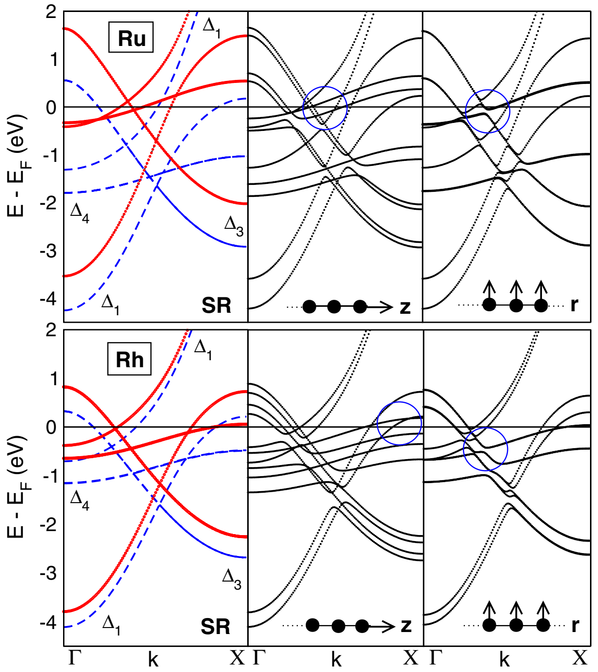

FIG. 2 (color online). Bandstructures of Ru and Rh chains at an interatomic distance of $d = 4.8$ a.u., calculated without SO (left panel) and with SO for two different magnetization directions (middle and right panels). Spin-up and spin-down in the case without SO (SR) are indicated by blue dashed and red solid lines, respectively. Large open (blue online) circles mark bands which give rise to orbital moments, as described in the text.

The directional dependence of the magnetization can be introduced by inclusion of SO. In the case of axial magnetization (middle panel of Fig. 2), two bands $\Delta_4^{\pm}$ with angular momenta $m_l = \pm 2$ are formed from the doubly degenerate spin-down Δ_4 band. The electron occupation of these bands is responsible for the actual value of $\mu_L(\mathbf{z})$. If the Δ_4^+ band is fully occupied, and the Δ_4^- band is not occupied at all, an orbital moment of $+2$ is obtained. Since only partial occupation is achieved, the orbital moments are $0.28\mu_B$ and $0.54\mu_B$ for Ru and Rh, respectively. In the latter case, the higher value of $\mu_L(\mathbf{z})$ is due to the full electron occupation of the Δ_4^+ band, in contrast to the Ru chain (encircled bands in the middle panel of Fig. 2). For radial magnetization (right panel), the generally smaller values of the in-plane orbital moments, $\mu_L(\mathbf{r})$, are due to the partial occupation of SO-split Δ_4-Δ_3 mixed bands (encircled bands in the right panel of Fig. 2). As a consequence of the larger band filling, the value of $\mu_L(\mathbf{r})$ is smaller for Rh than for Ru ($0.07\mu_B$ compared to $0.17\mu_B$). In a Pd chain the fully occupied Δ_4 bands lie well below the Fermi energy, giving rise to a small contribution to $\mu_L(\mathbf{z})$, while the larger values of $\mu_L(\mathbf{r})$ are due to the SO-split Δ_3 bands at the Fermi energy [7]. In general, the peculiar behavior of the orbital moments in 4*d* transition-metal MWs is due to an interplay of partial occupation of spin-orbit split Δ_3 and Δ_4 bands and their relative position with respect to the Fermi energy, attributed to the band filling. For example, the presence of the flat Δ_4 band at E_F will result in large values of $\mu_L(\mathbf{z})$.

Bare infinite monowires do not exist in nature. They are either deposited on a surface or created in a break junction. In either case, monoatomic metallic chains would have an interatomic distance *d* different from the calculated equilibrium values for freestanding wires. Therefore, we have investigated the behavior of the MAE, the spin and orbital moments as function of the distance *d*. In agreement with Spišák and Hafner [8] we found that Ru, Rh, and Pd monowires exhibit a FM ground state over a large range of interatomic distances. In general, an increase of the distance *d* leads to a pronounced increase of the spin moment (see Fig. 3) due to the reduced hopping, as explained above.

For Ru and Rh, already for $d > 5$ a.u., the spin moments saturate at their atomic-like values. The orbital moments gradually rise with *d*. For $d > 6.3$ a.u. giant values of $1.5\mu_B$ for $\mu_L(\mathbf{z})$ and $0.7\mu_B$ for $\mu_L(\mathbf{r})$ for both MWs are reached. An increase of *d* leads to a narrowing of the Δ_3, Δ_4 bands, and, eventually, bands with different angular momentum m_l become almost fully occupied or fully unoccupied, giving rise to a large value of the orbital moment. In case of Pd, for large distances, the *s* electron is transferred into the *d* shell, closes the *d* shell with 10 electrons and spin and orbital moments disappear [7]. In general, the influence of the SO on the spin moment can be seen only in cases where $\mu_S < 1\mu_B$.

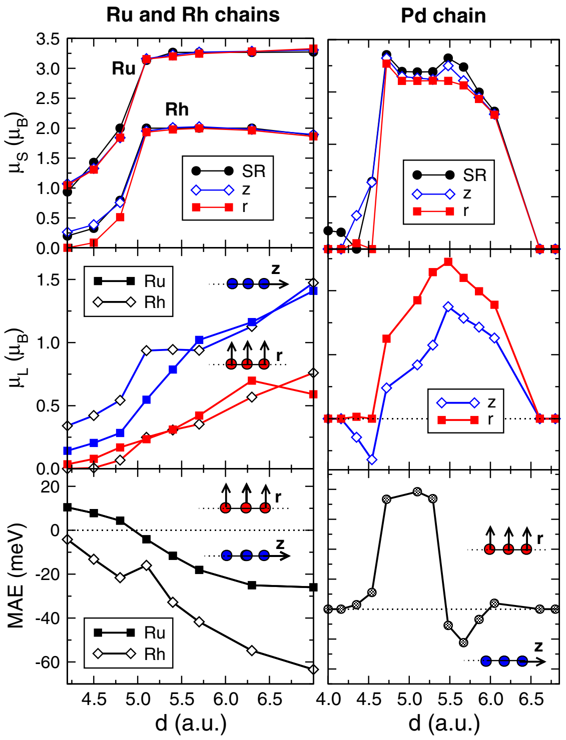

FIG. 3 (color online). Ferromagnetism in monoatomic chains of Ru, Rh, and Pd: MAE, spin, and orbital magnetic moments as a function of interatomic distance. Notice that the scale along the *y* axis is different for the left and right panels.

The combination of high values for spin and orbital moments with the large difference between $\mu_L(\mathbf{r})$ and $\mu_L(\mathbf{z})$ results in giant values of the MAE [25]. For example, already at $d = 5.5$ a.u., the MAE of the Rh chain reaches 40 meV/atom and gets as large as 60 meV/atom for $d = 6.3$ a.u.. While the monowire-substrate interaction often plays a crucial role for the magnetic properties of MWs [9], the large values of MAE found here suggest stable magnetization of the chains on various weakly interacting substrates such as insulating films or semiconducting surfaces [21,26]. In particular, the interatomic distance of a monowire deposited on typical surface ranges from 4.6 to 6.0 a.u., and in this interval the chain MAE changes drastically (Fig. 3). As already noticed in Fig. 1, when the values of $\mu_L(\mathbf{z})$ and $\mu_L(\mathbf{r})$ are close, a switch of the magnetization direction can occur as observed for Ru and Pd at $d = 5.0$ a.u. and $d = 5.4$ a.u., respectively. This peculiar behavior of the MAE can be used for tuning the magnetization direction by precise control of the interatomic distance, e.g., in a controllable break junction. This could lead to high values of the ballistic magnetoresistance without the need to change the magnetization of the leads or to apply an external magnetic field.

As compared to 4*d* chains, the magnetism of 5*d* transition-metal MWs is characterized by an even larger spin-orbit strength but generally smaller or even suppressed magnetic moments [6] due to the larger overlap of the 5*d* wave functions. For example, among the late 5*d* metals at their respective equilibrium lattice constants we found the largest MAE value for an Os MW reaching only 2 meV/atom and a spin-moment $\mu_S(\mathbf{z})$ of $0.36\mu_B$. At a strained interatomic distance of 6.3 a.u., where the values of the spin moments of ferromagnetic Os, Ir, and Pt chains are already well-saturated to $3.53\mu_B$, $2.39\mu_B$, and $1.13\mu_B$, respectively, the respective MAE values of 115, 60, and 44 meV/atom are—at least for Os—colossal in size and can exceed the record value of the Rh chain.

Summarizing, exchange split *d* bands in one-dimensional systems whose occupation can be altered significantly upon changing the lattice constant leads, together with a large spin-orbit splitting, to gigantic magnetic anisotropy energies for stretched freestanding chains of late 4*d* and 5*d* transition metals. These gigantic MAEs should stabilize the magnetic state in finite chains at comparatively high temperatures. Together with the structural stability of Ru, Rh, and Pd nanowires and breaking contacts observed experimentally [27,28] and predicted theoretically [29] for a variety of configurations, the experimental observation of the enhanced magnetism in these structures should be possible. The sensitivity of the 1D bands to band filling opens the possibility to tune the magnetization direction under strain and in this way to explore new magneto-transport properties.

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