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Change of cobalt magnetic anisotropy and spin polarization with alkanethiolates self-assembled monolayers

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Abstract

We demonstrate that the deposition of a self-assembled monolayer of alkanethiolates on a 1 nm thick cobalt ultrathin film grown on Au(111) induces a spin reorientation transition from in-plane to out-of-plane magnetization. Using *ab initio* calculations, we show that a methanethiolate layer changes slightly both the magnetocrystalline and shape anisotropy, both effects almost cancelling each other out for a 1 nm Co film. Finally, the change in hysteresis cycles upon alkanethiolate adsorption could be assigned to a molecular-induced roughening of the Co layer, as shown by STM. In addition, we calculate how a methanethiolate layer modifies the spin density of states of the Co layer and we show that the spin polarization at the Fermi level through the organic layer is reversed as compared to the uncovered Co. These results give new theoretical and experimental insights for the use of thiol-based self-assembled monolayers in spintronic devices.

Introduction

Self-assembled monolayers (SAMs) provide well-established means to chemically and physically modify metal surfaces [1, 2]. The engineering of properties such as wetting, adhesion, friction and reactivity has been the first area where this ability has been demonstrated. Moreover, SAMs also affect the electronic properties of metals, since the molecular dipoles inside the monolayer induce a change in the metal work function. This phenomenon can be exploited to improve the performance of hybrid metal/organic electronic devices, by lowering the energy barrier for charge injection [3, 4]. More recently, interfacial effects have also been shown to govern the response of organic spintronic devices [5–8]. In this context, SAMs are promising candidates with which to control the spin injection from magnetic electrodes into the organic layer [9]. The engineering of the interface is believed to be so important that a new discipline is expected to emerge, which has been labeled 'spinterface science' [10]. Moreover, a very small number of studies have suggested that spin polarized currents through a tunnel junction are peculiar to the presence of a SAM barrier [11, 12]. Meanwhile, understanding how an organic/ferromagnetic interface changes the magnetic behavior of the electrode (most notably its magnetic anisotropy energy, (MAE)) is a crucial missing part of this framework. The study of the impact of molecular adsorbates on the magnetism of thin films has been so far mainly limited to small molecules (such as H_2 or CO) physisorbed on a ferromagnetic layer [13–15] and only very rarely to more complex functionalized molecules [16]. However, it is expected that the chemisorption of molecular species would influence to a greater extent the properties of magnetic thin films, since the formation of a chemical bond or a charge transfer directly influences the electronic properties of the substrate [17]. This effect is also believed to cause the appearance *ex nihilo* of ferromagnetism in gold nanoparticles [18] and ZnO nanotubes [19] grafted to a SAM. Among the possible molecular components of

SAMs, *n*-alkanethiols occupy a privileged position because they are simple molecules which easily assemble to form compact and crystalline films. Furthermore, they are also very reactive species since the thiol head group (-SH) is capable of binding to many metals, including ferromagnetic metals [20, 21] by deprotonation (leading to a thiolate) and the formation of a sulfur–metal bond. In the following, all the alkanethiol layers are therefore assumed to be in the corresponding thiolate form when bound to a metallic surface.

Despite the considerable interest in SAMs on ferromagnetic surfaces, for both fundamental reasons and applied purposes, the investigation of the structure of monolayers and how they influence magnetic properties has been limited so far to very few, mainly theoretical, studies [21–23]. In this work, we have deposited octanethiols [$CH_3(CH_2)_6CH_2SH$] and dodecanethiols [$CH_3(CH_2)_{10}CH_2SH$] under ultra-high vacuum (UHV) conditions on thin Co films supported on a Au(111) substrate, as shown schematically in figure 1(a). Using scanning tunneling microscopy (STM), the growth of the monolayers on Co has been studied, and utilizing magneto-optical Kerr effect (MOKE) measurements, we have investigated how the SAM modifies the magnetic properties (notably the magnetic anisotropy) of the Co thin films, and find that it promotes an out-of-plane anisotropy. *Ab initio* density functional theory calculations of this complex system show that the main influence of the SAM is to modify the Co magnetic anisotropy, the interface magnetic moment and reverse the spin polarization at the Fermi level. The change of magnetocrystalline anisotropy is found to promote in-plane magnetization whereas the change of shape (dipolar) anisotropy (induced by the magnetization change) favors out-of-plane magnetization. As a consequence, the calculated global change of anisotropy is found to be very small, and the experimental change is attributed to a roughening of the Co layer, in good agreement with STM images taken before and after the deposition of the alkanethiolates.
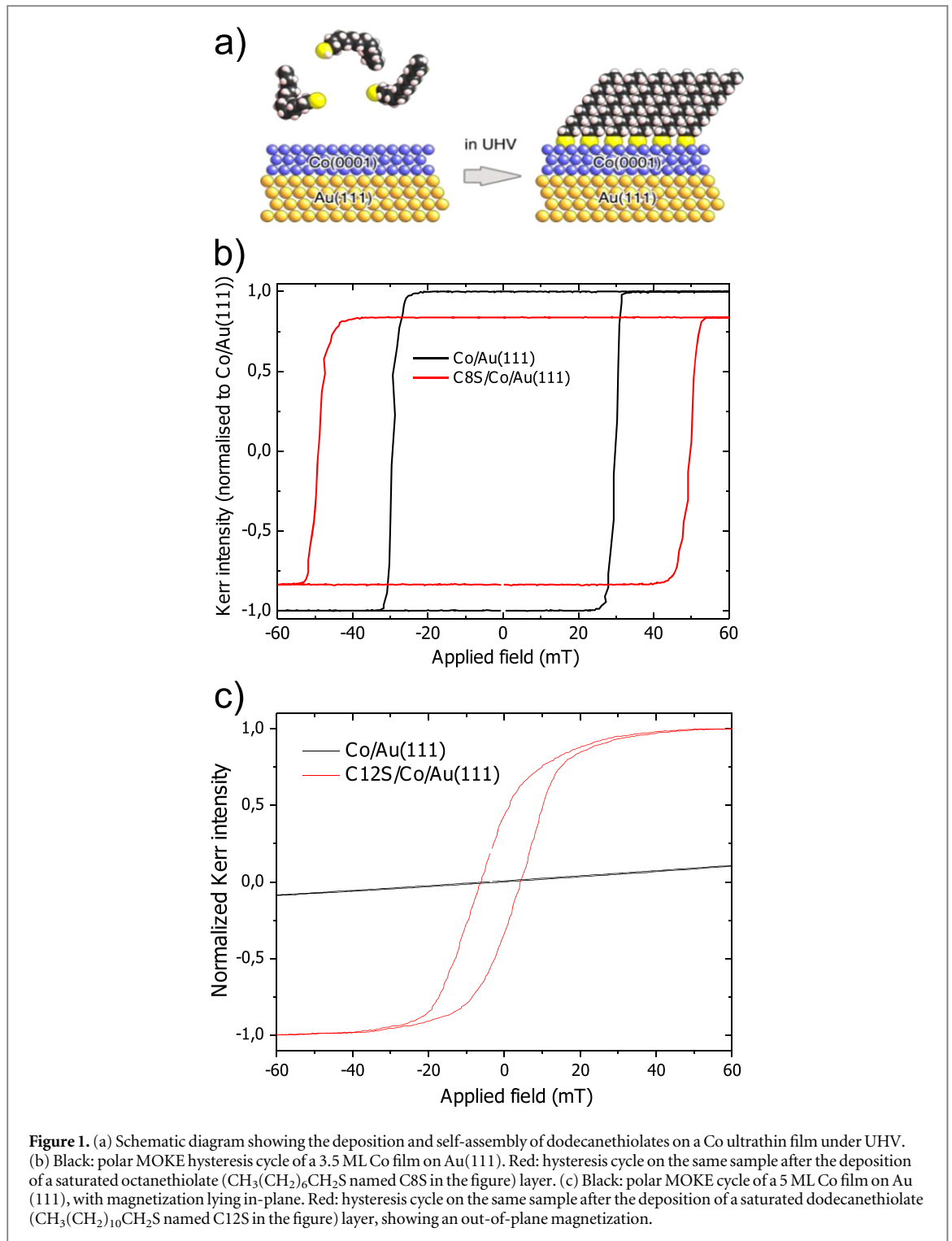
Methods

Experimental techniques
The self-assembly of alkanethiolates on Co is usually hindered by the reactivity of this metal. In an ambient atmosphere, Co readily oxidizes to form a passivation layer which inhibits the formation of sulfur–metal bonds. To avoid this problem, the deposition of thiols on thin Co films was performed directly under UHV conditions, with a base pressure lower than 10^{-10} mbar. The Au(111) substrate (purchased from Surface Preparation Laboratory, Zaandam, The Netherlands) was cleaned with repeated cycles of bombardment with Ar ions ($p_{Ar} = 2 \times 10^{-6}$ mbar, $V = 1$ kV, ionic current on target of 3 μA on a centimeter square area) followed by annealing at 750 K. Cobalt was evaporated by electron bombardment heating (Omicron EFM3 e-beam evaporator) of high-purity rods (Goodfellow, high-purity rod 99.99%, located at around 15 cm from the sample). A typical flux rate was 0.2 ML min^{-1}. The thickness of the Co films was determined by calibration on submonolayers using STM, giving rise to a typical error bar of ~20% on the absolute Co thickness. Dodecanethiols or octanethiols (Sigma-Aldrich, 98%) were evaporated directly in UHV with a simple homemade evaporator made of a clean tungsten filament dipped in the thiol solution and heated in vacuum at 570 K (checked by pyrometer) at few centimeters from the sample [24]. After 20 min of deposition, we checked by STM (VT-XA, Omicron, images recorded at a tunneling current of 20 pA and a voltage between 1 and 2 V) on Au(111) that we have obtained a fully saturated self-assembled monolayer with the characteristic $\sqrt{3} \times \sqrt{3}$ structure. This *in situ* technique allowed us to compare the magnetism of ultrathin Co films without and with a molecular overlayer, as sketched schematically in figure 1(a). Magnetization hysteresis loops were recorded with polar MOKE at room temperature. The optical setup consists of a 632.8 nm He–Ne laser (13 mW) and two Glan–Taylor almost crossed-polarizers. The detection is done with an amplified (10^8) photodiode. The magnetic field is generated *ex situ* by a Cu wire coil with a sweep rate of 1 Hz and a maximum applied field of 76 mT. The magnetic cycles shown in the following display the raw variation of the amplified photodiode voltage as function of the magnetic field intensity. A typical run of experiments can be performed in the same day and consist of the following: cleaning of the Au(111) substrate, deposition of a Co ultrathin film, STM image and magnetization cycle of this sample, deposition of the self-assembled monolayer, STM image and magnetization cycle of this new sample.

Calculation Details
The *ab initio* calculations have been performed with the Quantum ESPRESSO distribution [25] which makes use of a plane wave basis and pseudopotentials. The local density approximation (LDA) was used for electronic exchange and correlation. This choice was motivated by the knowledge that properties such as the MAE are very sensitive to the lattice constant, and the LDA proves to be more accurate than, for example, the generalized gradient approximation (GGA), in calculating the lattice constants of the metals used in this study. We first performed a set of calculations using scalar relativistic pseudopotentials, in order to obtain optimized geometries. For these calculations, plane wave cut-offs of 30 Ry and 300 Ry were used for the wavefunctions and

Figure 1. (a) Schematic diagram showing the deposition and self-assembly of dodecanethiolates on a Co ultrathin film under UHV. (b) Black: polar MOKE hysteresis cycle of a 3.5 ML Co film on Au(111). Red: hysteresis cycle on the same sample after the deposition of a saturated octanethiolate ($CH_3(CH_2)_6CH_2S$ named C8S in the figure) layer. (c) Black: polar MOKE cycle of a 5 ML Co film on Au (111), with magnetization lying in-plane. Red: hysteresis cycle on the same sample after the deposition of a saturated dodecanethiolate ($CH_3(CH_2)_{10}CH_2S$ named C12S in the figure) layer, showing an out-of-plane magnetization.

charge densities, respectively. Convergence was improved by making use of Marzari–Vanderbilt smearing with a width of 0.01 Ry. The interactions between valence electrons and the ionic cores were described using ultrasoft pseudopotentials [26]. Subsequently, calculations to determine the MAE were done using fully relativistic pseudopotentials [27] for all the elements. Ultrasoft pseudopotentials were used for all the elements except sulfur, for which a norm-conserving pseudopotential was used. For these calculations, higher plane-wave cut-offs, i.e. 40 Ry for wavefunctions, and 500 Ry for charge densities, were used in order to achieve the greater degree of accuracy required when calculating the MAE; this is because the MAE is a small quantity that is obtained by computing the difference between two large numbers. Most crucially, the convergence of the calculated value of MAE with respect to the number of *k*-points sampled in the Brillouin zone was checked carefully. We found that a $30 \times 30 \times 1$ Monkhorst–Pack sampling of the Brillouin zone sufficed to yield a converged value of the MAE. A lower smearing width of 0.0007 Ry was used for the MAE calculations.
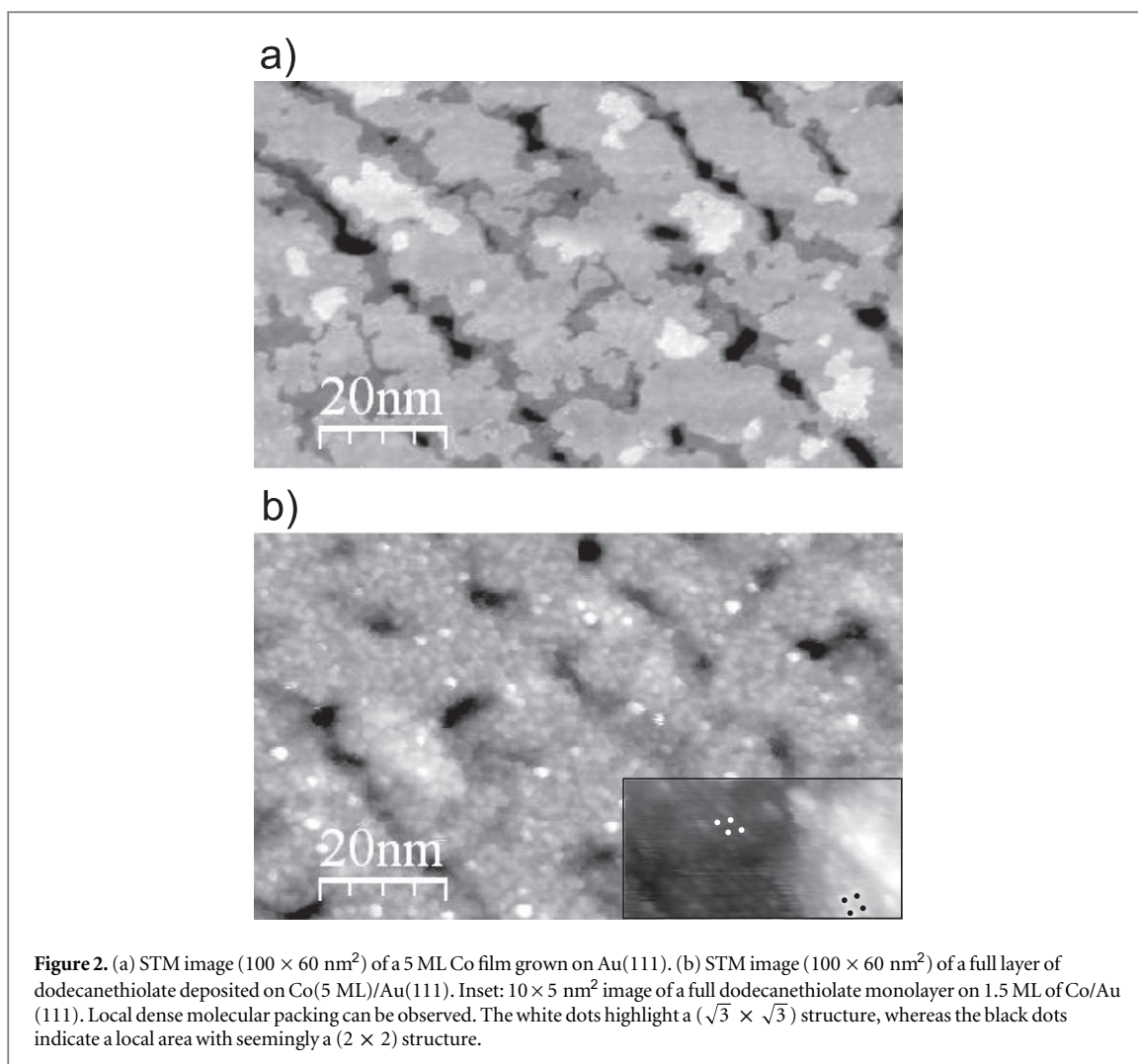
Results and discussion

The effect of octanethiolates and dodecanethiolates on the magnetism of Co thin films was first studied experimentally for a 3 ML film where it is known that Co shows an out-of-plane magnetization [28]. In a polar MOKE configuration, we are sensitive to the out-of-plane component of the magnetization. Therefore, a spontaneous out-of-plane magnetization (positive MAE) gives rise to an open and saturated hysteresis cycle while a spontaneous in-plane magnetization (negative MAE) gives rise to a reversible closed cycle. The 3 ML Co layer exhibits a well-saturated square hysteresis loop, with a coercive field H_c of around 29 mT (cf the black curve in figure 1(b)), typical of an out-of-plane magnetization. Upon the adsorption of octanethiolates, we see that the hysteresis loop maintains its squared shape (see the red curve in figure 1(b)), but H_c increases significantly, reaching a value of 49 mT for a fully covered surface, i.e. an increase by a factor of 1.7. In this experiment, we have taken great care to keep the magneto-optic calibration unchanged, and could measure a decrease of the magneto-optical signal by 16% (cf figure 1(b)). Assuming that the magneto-optical constant does not change upon the deposition of thiolates, this decrease can be interpreted as a magnetization change, which we will discuss further below in the light of *ab initio* calculations. It is worth noting that a similar experiment done on a 3.5 ML Co film covered with dodecanethiolates shows a similar increase of coercivity by a factor of 2.2. In general, the increase of coercivity can be due to several factors in ultrathin films: (i) imperfections in the film can cause traps capable of pinning the domain-wall motion, increasing the coercivity for a fixed sweep rate, (ii) an increase of the magnetic anisotropy, and (iii) an increase of the magnetic exchange [29]. In the present case, the magnetization direction does not change upon alkanethiolates adsorption, and it is therefore difficult to discriminate between these different factors, which can all be modified by the presence of the SAM. However, only a change of magnetic anisotropy is able to switch the direction of the spontaneous magnetization, what we demonstrate for a thicker Co film in the following. We therefore believe that the main reason for the increase of coercivity is an increase of the MAE.

To characterize more precisely the change of magnetism induced by a SAM composed of thiolates, we have deposited dodecanethiols on a 5 ML thick Co film, just above the critical thickness of the magnetization reorientation transition [28]. As can be seen in figure 1(c), the curve in polar geometry of a bare Co film is an unsaturated reversible cycle. The linear dependence on the field (see the black curve in figure 1(c)) represents a hard axis behavior, demonstrating that the easy axis of magnetization lies parallel to the film plane. Interestingly, upon deposition of a full monolayer of thiolates, there is a marked change in the shape of the curve; the cycle now becomes saturated and open (see the red curve in figure 1(c)), typical of a canted magnetization [30]. This means that the deposition of thiolates has switched the sign of the MAE, i.e. the direction of the easy axis, inducing a partial spin reorientation transition for this particular Co thickness. On this sample, we can unambiguously ascribe the change in magnetization cycles to a change of magnetic anisotropy.

In order to interpret these results, we have first studied the morphological change caused by the molecular deposition with *in situ* STM and Auger electron spectroscopy (AES). Figures 2(a) and (b) are STM images of a typical 5 ML Co film before and after the completion of a monolayer of dodecanethiolate, as checked by AES. Images have also been recorded for the 3.5 ML Co film and show very similar results. Upon comparing these two images, we can observe that the molecular layer induces some short-range roughness of atomic height, and a typical correlation length of ~3.5 nm. This molecular-induced corrosion is very similar to what has been observed previously for sulfur-based molecules on gold [31, 32]. At smaller length scales, we were not able to observe a long-range-ordered molecular structure, although we can observe easily, using the same tip, the characteristic $(\sqrt{3} \times \sqrt{3})$ structure obtained when dodecanethiolates or octanethiolates are deposited on Au (111). At low Co coverage, when part of the Au(111) surface is uncovered, we could observe locally some hexagonal molecular packing on Co with molecular orientations compatible with either a $(\sqrt{3} \times \sqrt{3})$ or a (2×2) structure (cf inset of figure 2(b)). It is worth noting that according to first principles calculations for methanethiolate on Co(0001) [21], the (2×2) and $(\sqrt{3} \times \sqrt{3})$ structures lie very close in energy, and for the case of sulfur adsorption on Co(0001), the (2×2) superstructure has been experimentally observed with LEED ([33]) and theoretically predicted to be the most stable structure [34]. In order to complete the characterization of the SAMs on the Co layers, we have performed AES. The ratio between the sulfur (151 eV) and carbon (273 eV) peaks increases for an octanethiolate layer on Co as compared to Au; this can be interpreted as arising from having a more disordered molecular layer on Co, in good agreement with the lack of molecular resolution observed in our STM images. We also find that the Co (53 eV) to Au(69 eV) ratio is constant within our experimental accuracy when Co is covered with the octanethiolate layer, indicating that only the Co surface layer is affected by the roughening indicated by STM.

In order to gain an understanding of the factors responsible for the changes in the magnetic hysteresis cycles, we have studied the magnetic properties of Co/Au(111), as well as methanethiolate on Co/Au(111), within the framework of spin polarized *ab initio* density functional theory. Due to the large size mismatch between Co and Au, it is not favorable for Co layers deposited on a Au(111) substrate to assume a pseudomorphic configuration;

Figure 2. (a) STM image (100×60 nm^2) of a 5 ML Co film grown on Au(111). (b) STM image (100×60 nm^2) of a full layer of dodecanethiolate deposited on Co(5 ML)/Au(111). Inset: 10×5 nm^2 image of a full dodecanethiolate monolayer on 1.5 ML of Co/Au (111). Local dense molecular packing can be observed. The white dots highlight a ($\sqrt{3} \times \sqrt{3}$) structure, whereas the black dots indicate a local area with seemingly a (2×2) structure.

instead, it has been found experimentally that thin films of Co on Au(111) are almost fully relaxed to the bulk Co nearest neighbor (NN) distance, with a NN distance of 2.56 Å [35]. Modelling such an incommensurate interface with *ab initio* density functional theory calculations would necessitate the use of a prohibitively large unit cell. We believe that the essential features of this structure can be retained by the use of, instead, a much smaller ($\sqrt{3} \times \sqrt{3}$) surface unit cell. In this cell, we place three gold atoms per layer, and four cobalt atoms per layer (cf figure 3(a)). In this way, we achieve a densification of the Co layers, with a NN distance between Co atoms of 2.49 Å instead of the value of 2.87 Å for a pseudomorphic layer. We point out however that the Co surface mesh is now rotated by 30° with respect to that of Au, which is not the case for the true experimental structure [35, 36]. We will show however that our model, by taking into account a non-pseudomorphic interface and a relaxed and densified Co layer, captures the essential physics and chemistry, and is closer to reality, regarding magnetic anisotropy, than previously used pseudomorphic models [37]. Moreover, this structure is found to be lower in energy than the pseudomorphic structure by around 0.4 eV/atom. In order to calculate the magnetic properties of an ultrathin Co film, we have considered either three or five Co atomic layers in such a rotated configuration, deposited on top of five Au layers. As the MAE is a very small and subtle quantity, we do not expect an absolute and quantitative comparison between theory and experiments, considering the various assumptions and approximations made in our measurements and calculations. However, we still believe that an observation of the change of MAE upon thiolate adsorption is still meaningful, as it is *a priori* not crucially dependent on the exact details of the structure of the Co/Au interface.

Further, though the experiments were performed with dodecanethiolates and octanethiolates, in our calculations we have modelled the adsorption of methanethiolate on Co/Au(111). This choice was governed mainly by issues concerning computational time, since the MAE calculations, which require dense Brillouin zone sampling, are extremely expensive. However, we note that previous calculations have shown that the binding between the thiolate and the metal surface changes very little upon changing the length of the alkyl chain [38]. Moreover, our experiments find the same magnetic behavior upon the adsorption of octanethiolates and
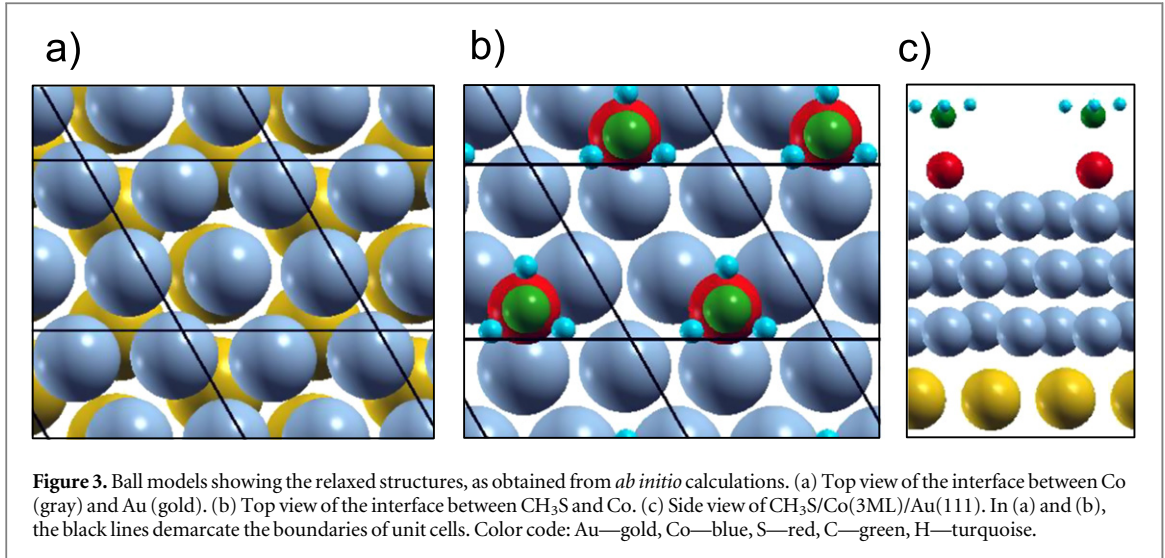
Figure 3. Ball models showing the relaxed structures, as obtained from *ab initio* calculations. (a) Top view of the interface between Co (gray) and Au (gold). (b) Top view of the interface between CH$_3$S and Co. (c) Side view of CH$_3$S/Co(3ML)/Au(111). In (a) and (b), the black lines demarcate the boundaries of unit cells. Color code: Au—gold, Co—blue, S—red, C—green, H—turquoise.

Table 1. Comparison of results from *ab initio* DFT calculations for the interlayer relaxations of Co layers (all in Å), for rotated hcp stacked Co(3 ML)/Au (111) and CH$_3$S/Co(3 ML)/Au(111). Index 1 denotes the surface Co layer. The values are obtained by averaging over all the Co atoms in the layer.

System	d_{12}	d_{23}	d_{34}
Co/Au(111)	1.88	1.91	2.29
CH$_3$S/Co/Au(111)	1.90	1.89	2.29

dodecanethiolates. For the structure of the methanethiolate layer, we have considered one CH$_3$S molecule per ($\sqrt{3} \times \sqrt{3}$) unit cell with the reconstructed Co layers on the Au substrate (cf figure 3(b)). Note that this unit cell is actually a (2×2) cell for the Co layers, which has been calculated to be a possible stable structure [22], and has been locally observed by STM in our experiments. We find that the hexagonal-close-packed (hcp) hollow site is the most stable one for the chemisorption of CH$_3$S. Moreover, we find that the molecule binds in a symmetric configuration, with a S–C bond of length 1.81 Å oriented perpendicular to the surface (cf figure 3(c)). The mean S–Co bond length is 2.09 Å.

In order to discuss possible magneto-elastic contributions to the MAE [14], we first compare the interlayer distances in the Co film with and without the molecular layer. Table 1 summarizes these distances for the case where the Co layer is 3 ML thick; we observe that the vertical relaxations in the Co layer are, on average, almost unaffected upon the adsorption of thiolates.

Next, we have theoretically computed the magnetic anisotropy energy of the Co/Au system. Two contributions to the MAE are important: the magnetocrystalline anisotropy energy K_{mc}, and the dipolar (shape) anisotropy energy K_d. In order to compute K_{mc}, we need to calculate the difference in the contribution from spin–orbit interactions to the total energy of the system when the magnetization lies in the surface plane, and when it points perpendicular to it. The sign convention is such that a positive value of the MAE indicates that the easy axis is out-of-plane, whereas a negative value indicates that it lies in-plane. We have carried out these calculations at two thicknesses of Co, 3 ML and 5 ML. We have determined that we obtain values of K_{mc} that are converged (to within a few %) upon using a $30 \times 30 \times 1$ k-point mesh.

Our results for the mean magnetic moment $\langle \mu_S \rangle$ (averaged over all the Co atoms in the slab), K_{mc}, K_d, and $K_{\text{tot}} = K_{mc} + K_d$, are given in table 2. We obtain $K_{mc} = 156 \, \mu\text{eV/Co}$ atom for 3 ML of Co/Au(111) and $K_{mc} = 64 \, \mu\text{eV/Co}$ atom for 5 ML of Co/Au(111). These positive values have to be supplemented with the shape anisotropy energy density in the ultrathin film limit, $K_d = -\frac{1}{2}\mu_0 \langle M_S \rangle^2$, where $\langle M_S \rangle$ is the average spin moment per unit volume, and μ_0 is the permeability of free space. We obtain a value of $K_d = -82 \, \mu\text{eV/Co}$ atom for 3 ML Co/Au(111), and $K_d = -81 \, \mu\text{eV/Co}$ atom for 5 ML Co/Au(111). Therefore, upon computing K_{tot}, we find that the value for the total MAE changes from $+74 \, \mu\text{eV/Co}$ atom for 3 ML Co/Au(111) to $-17 \, \mu\text{eV/Co}$ atom for 5 ML Co/Au(111). The most significant result here is that the MAE changes sign upon going from three layers of Co/Au(111) to five layers of Co/Au(111), with the easy axis switching from being out-of-plane to in-plane. This is in good agreement with our experimental findings (recall the differently shaped black curves in figure 1(b) and

Table 2. Results from *ab initio* density functional theory calculations for the values of the average spin moment $\langle \mu_S \rangle$ in μ_B/Co atom, and of the magnetocrystalline anisotropy energy density K_{mc}, the shape anisotropy energy density K_d and the total magnetic anisotropy energy density K_{tot} in μeV/Co atom. Positive values correspond to an out-of-plane easy axis.
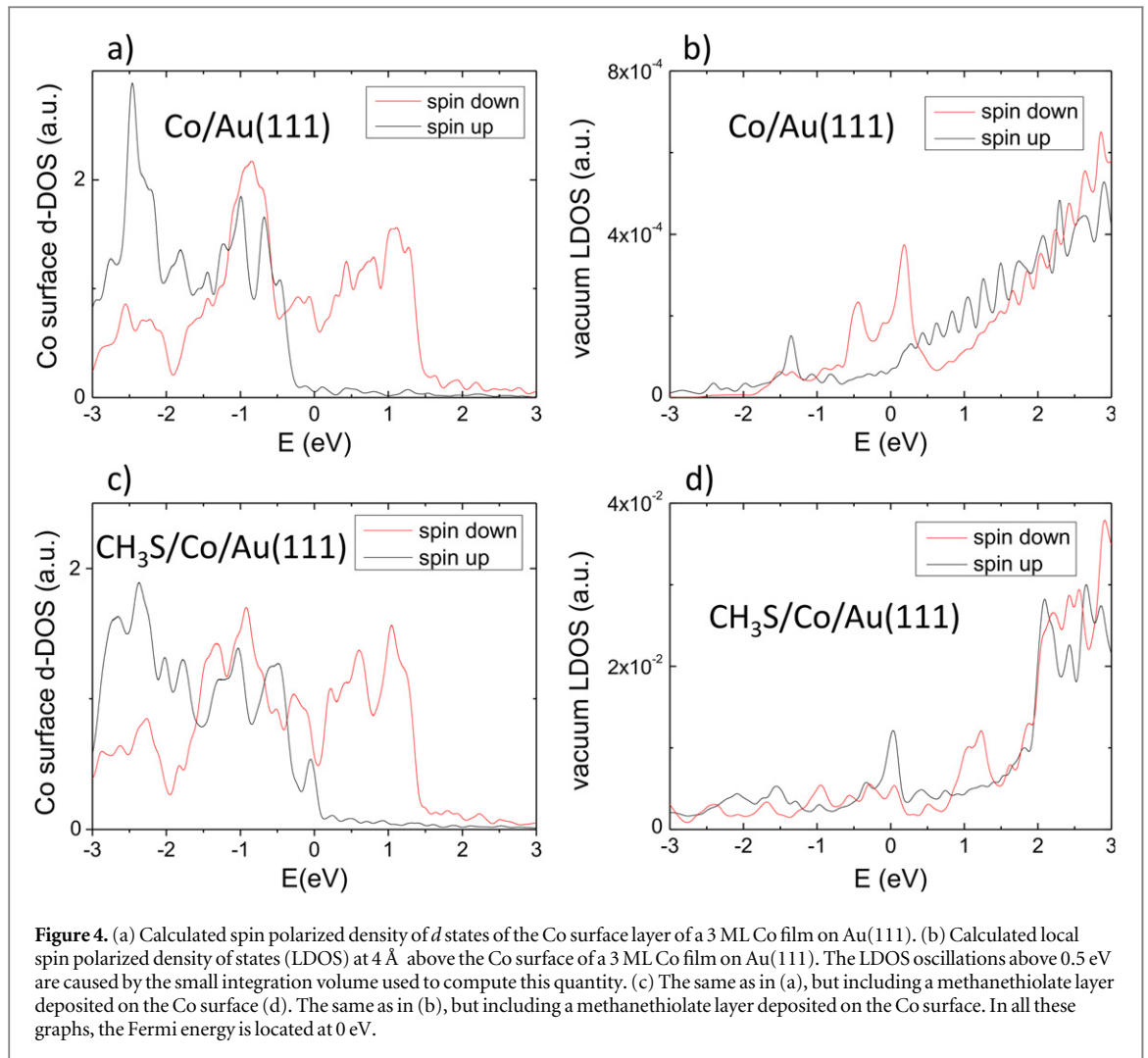
System	$\langle \mu_S \rangle$	K_{mc}	K_d	K_{tot}
Co(3ML)/Au(111)	1.62	156	−82	74
CH$_3$S/Co(3ML)/Au(111)	1.48	122	−68	54
Co(5ML)/Au(111)	1.60	64	−81	−17
CH$_3$S/Co(5ML)/Au(111)	1.53	60	−76	−16

(c)) and is a great improvement on the results from previous theoretical studies that considered a pseudomorphic structure [37].

Next, we consider what happens when a layer of methanethiolate is deposited on top of the Co layers on Au (111). Both the magnetocrystalline anisotropy K_{mc} and the shape anisotropy K_d are affected upon deposition of the SAM. Note that in this case, the change in shape (dipolar) anisotropy does not arise from a change of shape of the system, but from the decrease of the magnetic moments, as we will show below. As we can see from the numbers in table 2, the values of K_{mc} reduce (become less positive) upon deposition of the methanethiolate layer, i.e. if one considers this contribution alone, the magnitude of the MAE is decreased, and the tendency for the easy axis to be out-of-plane, while maintained, is slightly reduced. Next, we consider how K_d is affected. For the uncovered 3 and 5 ML Co layers, surface Co atoms have a magnetic moment of 1.67 μ_B and 1.69 μ_B respectively. Sub-surface Co atoms have a moment of ∼1.59 μ_B for the 3 ML case and ∼1.61 μ_B, ∼1.55 μ_B, ∼1.57 μ_B and ∼1.58 μ_B for the four sub-surface layers of the 5 ML case (starting from the surface). These values change upon adsorption of the thiolate layer. For the CH$_3$S/Co/Au(111) system, there are two types of surface Co atoms, i.e. those directly bonded to sulfur atoms, having lower magnetic moments of ∼1.20 μ_B, and those not bonded to sulfur, having a larger magnetic moment of 1.74 μ_B. The sub-surface atoms are also affected, with the Co atom directly below the S atom having a moment of 1.66 μ_B, and the other atoms in the subsurface Co layer having a moment of 1.49 μ_B. The Co layer in contact with Au is more-or-less unaffected, with a homogeneous magnetic moment of around 1.58 μ_B. The net effect of all these changes is that upon deposition of the SAM, the mean magnetic moment per Co atom decreases from 1.62 to 1.48 μ_B for the 3 ML Co/Au(111) system, and from 1.60 to 1.53 μ_B for the 5 ML Co/Au(111) system. Since the Co–Co in-plane distance remains constant, and interplanar distances are essentially unaltered by the deposition of the SAM, this implies that $\langle M_S \rangle$, and therefore the magnitude of K_d, decreases upon thiolate deposition. Finally, the total MAE per atom, K_{tot}, is summarized in table 2, showing a slight decrease with the SAM capping (−20 μeV/atom) for the 3 ML Co film and a very slight increase (+1 μeV/atom) for the 5 ML film.

These results from *ab initio* calculations can be compared, at least qualitatively, to our experimental results. First, upon thiolates deposition, the total calculated magnetization is decreased by 8% for a 3 ML Co film; this can be compared with our measurement of a 16% decrease of the MOKE signal (cf figure 1(b)). We see that the qualitative variation is well described by the calculations, although underestimated. This discrepancy could be due to a small change in the magneto-optical constant induced by the thiolates layer, even if the Co *d* states are only slightly modified (except close to the Fermi level, as discussed further below). It could also be due to morphological and structural differences. Indeed, the calculations only consider a perfect (2 × 2) structure with a flat Co surface, whereas the experiments show a rather disordered molecular layer, together with a roughening of the Co layer. Regarding the change in MAE, the *ab initio* results clearly indicate that the hybridization with sulfur atoms decreases the perpendicular magnetocrystalline anisotropy, rather strongly for a 3 ML film. However, this tendency is partially counterbalanced by the decrease of the in-plane shape anisotropy induced by the reduction of the magnetic moments. For a 5 ML film, this balance is almost perfect, leading to a very small change of the total MAE. The experimental observation of a slight increase of the perpendicular anisotropy for the 5 ML film upon thiol deposition could possibly be due to the fact that the actual decrease of the magnetic moments is more pronounced than that obtained in the calculations (as in the case of the 3 ML film), giving rise to a smaller shape anisotropy. Moreover, the observed roughening of the magnetic layer can also be expected to slightly increase the perpendicular anisotropy [39].

Finally, we discuss the electronic properties of such hybrid ferromagnetic/organic systems. Self-assembled monolayers of alkanethiolates are of interest for spintronics as they can be used to create a well-defined tunneling barrier, which can be functionalized by chemical terminal groups so as to obtain enhanced properties. It is therefore of interest to compare the evanescent spin-polarized density of states through such a molecular layer as compared to the same quantity through a vacuum. To do so, we have computed the local spin-up and spin-down density of states at ∼4 Å above the Co surface, without and with the methanethiolate layer (note that

Figure 4. (a) Calculated spin polarized density of *d* states of the Co surface layer of a 3 ML Co film on Au(111). (b) Calculated local spin polarized density of states (LDOS) at 4 Å above the Co surface of a 3 ML Co film on Au(111). The LDOS oscillations above 0.5 eV are caused by the small integration volume used to compute this quantity. (c) The same as in (a), but including a methanethiolate layer deposited on the Co surface (d). The same as in (b), but including a methanethiolate layer deposited on the Co surface. In all these graphs, the Fermi energy is located at 0 eV.

the terminal H atoms of the methanethiolate molecule are at a distance of ∼3.65 Å from the Co surface). As shown in figures 4(b) and (d), the presence of the molecular layer drastically changes the spin-polarized density of states close to the Fermi level. Calculating the spin polarization $P = (n_{up} - n_{down})/(n_{up} + n_{down})$, where n_{up} and n_{down} are the up-spin and down-spin charge densities, respectively, we find that P goes from −48% for uncovered Co to +41% through the thiolates layer. This inversion of the sign of the spin polarization is very similar to what has been calculated for carbon conjugated molecules on Fe [6], but has a different origin. In our case, we find that this inversion directly comes from the last Co layer which shows a pronounced resonance for spin-down that switches to spin-up when hybridized with the methanethiolates, as shown in figures 4(a) and (c) where we display the contribution of the Co d states of the last Co plane, without and with a methanethiolate layer. Note that the decay of these states in the vacuum is spin-dependent so that the inversion of spin polarization induced by the methanethiolate layer occurs only in the vacuum.

Summary and conclusions

We have studied the change of magnetic properties of cobalt thin films, upon covering them with a self-assembled monolayer of alkanethiolates, using a combination of scanning tunneling microscopy, magneto-optical Kerr effect experiments, and *ab initio* density functional theory calculations.

First, we have confirmed, both experimentally and theoretically, that there is a spin reorientation transition on going from 3 ML to 5 ML of Co deposited on Au(111), with the easy axis switching from being out-of-plane to in-plane.

Next, we have found that an important effect of thiolate deposition on ferromagnetic surfaces arises from the quenching of magnetic moments. This in turn reduces the tendency for the easy axis to lie in-plane, upon considering the contribution from shape (dipolar) anisotropy alone. This effect may or may not be countered by changes in the magnetocrystalline anisotropy. We have seen that changes in both the magnetocrystalline

anisotropy and the shape anisotropy are important and similar in magnitude, though in some cases they cancel each other out.

Importantly, we have presented evidence that the effect of thiolate deposition on a ferromagnetic substrate such as Co/Au(111) can depend sensitively on the thickness of the ferromagnetic layer.

Our experiments indicate that the thiolate layer induces a partial spin reorientation transition for a 5 ML Co film, promoting a small out-of-plane anisotropy. The *ab initio* calculations show that though the magnitude of the shape anisotropy decreases on thiol deposition for this system, reducing the tendency for the easy axis to lie in-plane, the net effect of thiolate deposition on a 5 ML Co film is negligible regarding magnetic anisotropy.

Taking together the totality of the results presented here, we conclude the influence of a thiolate layer on the magnetic anisotropy of a Co film is a delicate effect, and that taking into account the complexity of the true interface (including such factors as disorder and roughening) is certainly necessary to perfectly describe this subtle quantity.

Our *ab initio* calculations also show an inversion of the spin polarization at the Fermi level through the molecular layer; this provides an initial basis for the understanding of spin transport through such organic layers.

We believe that this work, by giving new insights on the interface properties of cobalt/thiolates, should be of interest to the general growing field of molecular spintronics using self-assembled monolayers.

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