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We demonstrate that a C_{60} overlayer enhances the perpendicular magnetic anisotropy of a Co thin film, inducing an inverse spin reorientation transition from in plane to out of plane. The driving force is the C_{60}/Co interfacial magnetic anisotropy that we have measured quantitatively *in situ* as a function of the C_{60} coverage. Comparison with state-of-the-art *ab initio* calculations show that this interfacial anisotropy mainly arises from the local hybridization between C_{60} p_z and Co d_{z^2} orbitals. By generalizing these arguments, we also demonstrate that the hybridization of C_{60} with a Fe(110) surface decreases the perpendicular magnetic anisotropy. These results open the way to tailor the interfacial magnetic anisotropy in organic-material–ferromagnet systems.

The use of organic materials in spintronic devices has recently raised a lot of interest. Large spin diffusion time in organic materials combined with complex couplings at the interfaces lead to very large magnetoresistance [1,2]. C_{60} is one of the model molecules that has been used so far to evidence the room temperature magnetoresistive effect for relatively thick layers [3]. More recently, peculiar interactions between a molecular layer and a cobalt electrode allowed for the demonstration of magnetoresistive behavior with a single magnetic electrode [4]. Despite the numerous transport measurements reported in various molecular spin-valve devices, only little is known on the effect of organic-material–ferromagnetic interfaces on the device performance, especially regarding magnetic anisotropy energy (MAE) [5].

It is known that MAE of a thin magnetic layer can be seriously affected by the interface with nonmagnetic layers. The influence of carbon based materials was believed to be small because of their low spin-orbit coupling constant but recent works have pointed out that the out-of-plane MAE is enhanced at a graphene-Co interface [6–8]. However, a quantitative measurement and the understanding of such an influence of carbon based overlayers on the MAE is still missing.

In this Letter, we demonstrate for the first time by *in situ* and real time control of thin film magnetic properties under a molecular deposition that a strong interfacial magnetic anisotropy can increase [C_{60}/Co(0001)] or decrease [C_{60}/Fe(110)] the perpendicular magnetic anisotropy (PMA). These results are analyzed and explained by state-of-the-art *ab initio* calculations where

we decompose the magnetic anisotropy on the different d orbitals of Co and Fe. The favored hybridization between metallic d_{z^2} and carbon p_z orbitals at the interface explains the experimental findings and gives a simple and predictive view of the interfacial magnetic anisotropy between a $3d$ ferromagnet and an organic layer, which is of crucial importance for the future development of organic spintronics.

An *in situ* ultrahigh vacuum polar magnetooptical Kerr effect (MOKE) setup was used to measure magnetic cycles during the deposition of C_{60} on Co/Au(111) and Fe/Au(111) ultrathin films. The magnetic cycles were recorded every 20 s with a magnetic field applied parallel to the surface normal with a sweep rate of 1 Hz generating a maximum field of 68 mT. It is known that Co on Au(111) undergoes a spin reorientation transition (SRT) from out of plane to in plane at a Co thickness t_c of 4.2 ML [9,10]. This value was used as a calibration of our Co thickness, in good agreement with STM and Auger electron spectroscopy results. To calibrate the thickness of C_{60} molecules, we used scanning tunneling microscopy (STM) images of submonolayer deposition on the Au(111) surface [11]. A monolayer (ML) of C_{60} is therefore defined as a dense hexagonal packing obtained on Au(111) [12]. However, STM images of C_{60} on the Co film (cf. top inset of Fig. 1) show a defective layer with a less dense packing. Therefore, analyzing the molecular surface density, we found that the Co surface is fully covered by C_{60} around 0.75 ± 0.05 ML.

To study the change in magnetism of Co films upon molecule deposition, experiments were performed both below and above t_c. The experiment summarized in Fig. 1
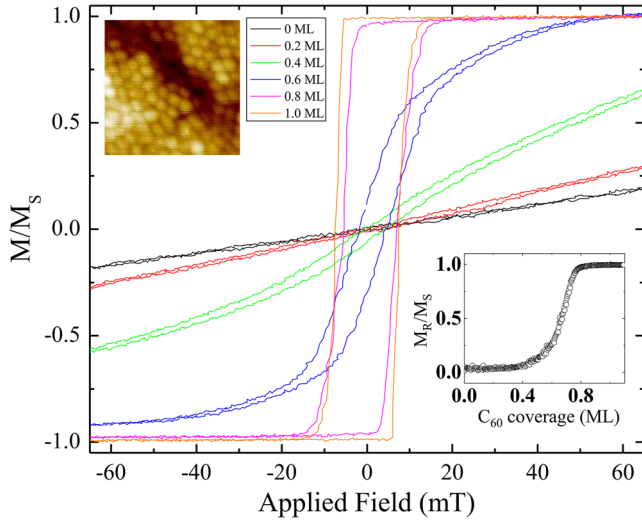
FIG. 1 (color online).   Raw hysteresis cycles measured during the deposition of C_{60} on 5.5 ML Co/Au(111) in a polar MOKE configuration. Bottom inset: Graph of the remanent magnetization M_R over the saturated magnetization M_S as a function of the C_{60} thickness. Top inset: Typical STM image after the deposition of 1 ML of C_{60} on 5.5 ML Co/Au(111) (12×12 nm^2, 1.0 V, 20 pA).

on a 5.5 ML Co film demonstrates that the magnetization switches from in plane to out of plane, showing a significant change in MAE with C_{60} coverage (cf. movie, Ref. [11]). The bottom inset shows the squareness (M_R/M_S, i.e., ratio of the remanent magnetization over saturated magnetization) of the cycles as a function of the C_{60} coverage, inducing an abrupt inverse SRT. Thus the C_{60} layer induced a PMA that needs to be quantified and understood.

Another indirect observation of this rise in MAE is the magnetic behavior of a 3.2 ML Co film that keeps an out-of-plane magnetization with the C_{60} overlayer but shows a modified coercive field H_c. Results are summarized in Fig. 2(a), which displays an increase of H_c by a factor larger than two with C_{60} coverage. This increase in coercivity is indirectly related to an increase of the out-of-plane magnetic anisotropy, although a quantitative determination is difficult because magnetic exchange could also play a role [13]. We also plot in Fig. 2(a) the variation of the saturated MOKE signal as a function of the C_{60} coverage. Assuming a constant magnetooptical constant, this can be interpreted as a slight decrease of the total Co film magnetic moment (given in absolute value measured independently by x-ray magnetic circular dichroism, [11]) [14].

To obtain a quantitative determination of the MAE variation with C_{60} deposition, we have performed hard axis magnetometry for Co films well above t_c, i.e., still in plane with a full fullerene layer. In this case, the saturation field is given by the anisotropy field $H_K = 2K_{\mathrm{eff}}/\mu_0 M_S$ where K_{eff} is the total effective anisotropy of the Co film.
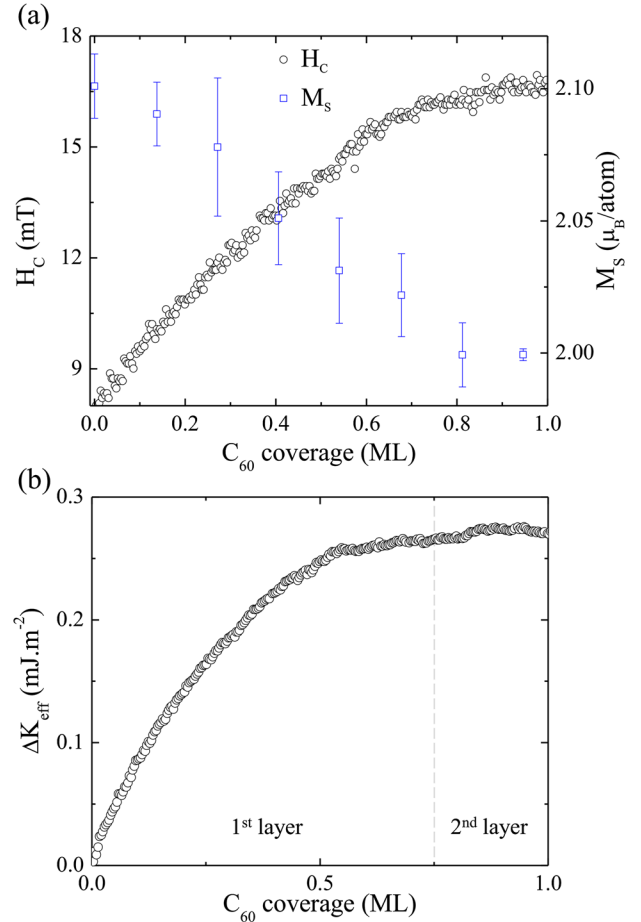

FIG. 2 (color online).   (a) Variation of H_C and M_S as a function of C_{60} coverage for a 3.2 ML Co film. (b) Interfacial magnetic anisotropy variation with C_{60} coverage for a 6.4 ML Co film.

As our *in situ* magnetic field is not high enough to saturate these reversible cycles, we extract H_K from the slope of the individual in-plane cycles and the saturation magnetization value. The latter is calibrated by an extrapolation of the saturated cycles measured for Co thickness below t_c. We find for our Co/Au(111) system, a surface anisotropy term $K_S = 0.6 \pm 0.1$ mJ m^{-2} and a volume anisotropy $K_V = -800 \pm 100$ kJ m^{-3} [11], in good agreement with the literature [10,15]. The change of MAE, expressed in surface anisotropy units, is plotted as a function of the C_{60} coverage for a 6.4 ML Co film in Fig. 2(b). This variation is linear with the coverage at low coverage and saturates around 0.7 ML. This corresponds exactly to the completion of a full fullerene layer, as determined by STM. For higher coverage, C_{60} molecules adsorb on a second layer, without direct interaction with Co atoms. We can therefore only ascribe this MAE change to an interface effect induced by the hybridization between C_{60} and Co. The interface anisotropy is around 0.3 mJ m^{-2}, i.e., around a half of the Co/Au anisotropy. This value is not negligible, especially if one considers that only a small fraction of the
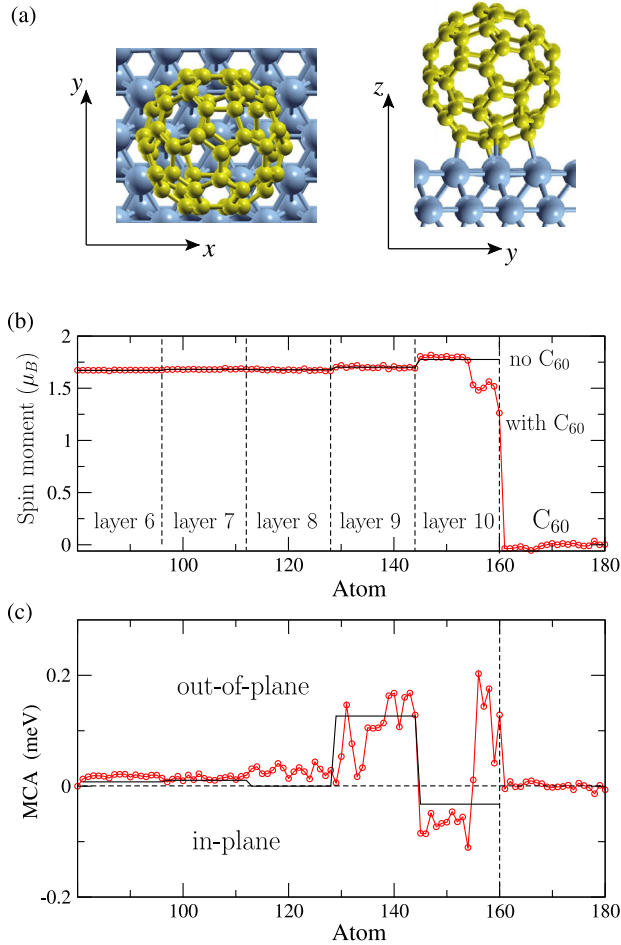
(a)

(b)

(c)

FIG. 3 (color online). DFT results for a 10-layer Co slab covered with C_{60} molecules: (a) lowest energy adsorption configuration of C_{60} monolayer; (b) atomic spin moments for the Co slab with (red open circles) and without (black solid curve) C_{60} molecules. There are 16 Co atoms per layer due to the 4×4 in-plane periodicity. Only contributions from the five outer Co planes close to C_{60} monolayer are shown; (c) atomically resolved MCA for the same two cases as in (b).

surface atoms are hybridized due to the spherical geometry of the C_{60} molecule [6 over 16 for a dense packing as shown in Fig. 3(a)] and that carbon is a light material with a low spin-orbit coupling constant. In the following, we give an atomic scale interpretation of this interfacial anisotropy in light of *ab initio* calculations.

We have performed density functional theory (DFT) calculations using the plane-wave electronic structure package QUANTUM-ESPRESSO [16]. Since the realistic atomic structure of Co films on a Au(111) substrate is experimentally complex and not perfectly known, we have chosen to simulate this system by a thick enough hcp Co slab containing 10 atomic layers with C_{60} molecules adsorbed on one side of the slab (possible effects of the underlying Au substrate are thus neglected for simplicity). A 4×4 in-plane periodicity is used resulting in C_{60}-C_{60} in-plane separation between the closest carbon atoms of

about 3.2 Å. Our goal is to look at the local change in magnetic anisotropy of Co atoms close to the C_{60} molecular layer. Such a thick 10-layer Co slab is necessary to reduce finite-size effects. In particular, the magnetic anisotropy of surface Co atoms was found to be rather sensitive to the slab thickness, both in sign and magnitude, as demonstrated for 5-, 10-, and 15-layer Co slabs [11].

To determine the adsorption geometry of C_{60} molecules we performed atomic relaxations using a thinner 5-layer Co slab. In both cases with and without C_{60} on the Co slab, the first three layers were fixed at their bulk positions while the outer layers were allowed to relax to minimize the total energy.

The most stable configuration shown in Fig. 3(a) corresponds to C_{60} molecules bound by a pentagon-hexagon edge to a Co surface atom [14]. Figure 3(b) shows atomic spin moments for a clean 10-layer Co slab (black curve) and for the same slab covered with C_{60} molecules (red open circles). Since the influence of the C_{60}/Co interface is vanishingly small after four Co layers, we only display the results for the five outer Co layers. One can clearly see that the Co magnetism is much affected by C_{60}, similarly to Cr [17] and Fe [18]. In particular, spin moments of the six Co atoms making bonds with C_{60} (Co atoms numbered as 155–160) are strongly reduced, dropping down to $\sim 1.25 \mu_B$ for the atom just beneath the C_{60} (Co atom number 160). On the contrary, we find that the C_{60} molecule gets slightly polarized with $-0.23 \mu_B$ in total [17].

We define MAE as the difference in total energies between in-plane and out-of-plane magnetic configurations, $E_\parallel - E_\perp$. The total MAE has two contributions, namely: (i) magnetocrystalline anisotropy (MCA) due to spin-orbit coupling (SOC) and (ii) shape anisotropy due to dipole-dipole magnetic interactions. We first discuss the MCA and will briefly address the shape anisotropy at the end of this section. In our DFT calculations, the spin-orbit coupling, crucial for MCA, is taken into account via fully relativistic pseudopotentials which are generated by solving the atomic Dirac equation for each atomic type. The MCA is then calculated within the force theorem approach, as implemented recently in Ref. [19].

In Fig. 3(c) we present atomically resolved MCA. For a clean slab (black line), the MCA values from the five outer planes sum up to the total value of ≈ 1.8 meV, thus favoring the out-of-plane magnetization direction. Upon adsorption of C_{60} molecules (red open circles), the overall out-of-plane MCA is further enhanced by ≈ 0.9 meV. Importantly, this enhancement is mainly provided by the six Co atoms directly involved in Co-C_{60} bonding (numbered as 155–160) that show locally an increase of anisotropy by about 0.2 meV/atom, which is a quite significant value. Their bonding to C_{60} has thus a very strong effect reversing their preferable magnetization axis from the in-plane to out-of-plane direction.
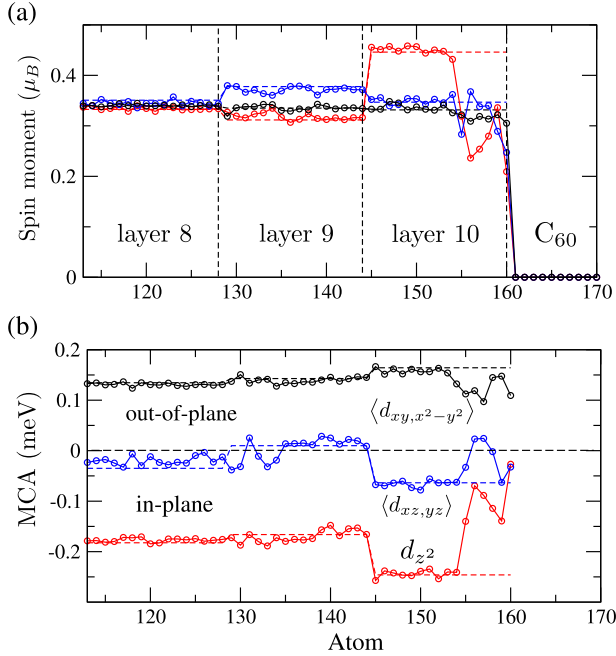
FIG. 4 (color online). d orbital decomposition of (a) atomic spin moments and (b) MCA for the 10 layers Co slab, pure (dashed lines) and covered with C_{60} molecules (solid lines). The results for three Co layers close to C_{60} molecules are only presented. Because of symmetry, contributions from different orbitals in $\{d_{xz,yz}\}$ and $\{d_{xy,x^2-y^2}\}$ pairs are very similar so that their averaged values are presented for simplicity.

In order to interpret the influence of C_{60} on local magnetism, we present spin moments in Fig. 4(a) and MCA in Fig. 4(b) decomposed over the different Co d orbitals (only the data for three Co layers close to C_{60} are shown for simplicity) for the bare Co and C_{60} on Co. Interestingly, from Fig. 4(b) we notice that for a pure Co slab, differently oriented d orbitals favor different magnetic orientations. In particular, the d_{xy,x^2-y^2} orbitals, parallel to the slab surface, show strong out-of-plane anisotropy, while the d_{z^2} orbital, perpendicular to the slab, favors the in-plane orientation (the other $d_{xz,yz}$ orbitals show intermediate values). Upon C_{60} adsorption, all the contributions at Co atoms bound to C_{60} get suppressed in magnitude. However, the degree of this reduction depends on the hybridization strength of the corresponding orbital with the C_{60} states: evidently, it is the strongest for the out-of-plane oriented d_{z^2} orbital and the smallest for the in-plane d_{xy,x^2-y^2} states. As a result of this unbalance, the overall MCA for these Co atoms appears to enhance strongly, favoring the out-of-plane orientation. The same argument is valid for spin moments: their reduction at Co atoms bound to C_{60} is essentially due to the suppression of the d_{z^2} contribution, as clearly demonstrated in Fig. 4(a).

Finally, we discuss shape anisotropy, the other contribution to magnetic anisotropy, which favors the in-plane magnetic orientation. It is calculated directly from atomic

spin moments as those presented in Fig. 3(b) [11]. For a 5-layer Co film, we find a value of -7.5 meV per 4×4 unit cell, that drops to -6.9 meV when covered with C_{60}. This decrease of the shape anisotropy magnitude is perfectly consistent with the decrease of the mean magnetization calculated in Fig. 3(b).

Quantitatively, we find for a 5 ML slab containing 16 Co atoms per atomic plane an overall increase of the out-of-plane magnetic anisotropy of 1.5 meV (0.9 meV for magnetocrystalline and 0.6 meV for dipolar anisotropies), i.e., around 19 μeV/atom if homogeneously averaged over all the Co atoms. However, this magnetic anisotropy increase is mainly due to interfacial atoms, as shown in Fig. 3(c). Averaged over the interfacial layer, it leads to almost 0.1 meV/atom or, converted in international units $\Delta K_{\mathrm{eff}} = 0.27$ mJ m^{-2}, in good agreement with our experimental measurement.

We believe that the theoretical arguments put forward to explain the experimental finding are rather general and can be applied to other metal-molecule interfaces. If the d_{z^2} surface component of the MCA favors in-plane (out-of-plane) magnetization, the hybridization with C_{60} will enhance out-of-plane (in-plane) magnetization. We have therefore performed a series of DFT calculations to determine the atomically and orbital resolved MCA of various bare surface orientations and magnetic elements. We predict that the densest surface of iron [Fe(110)] has an opposite behavior to the Co(0001) surface since the contribution of the d_{z^2} orbital to the surface MCA is clearly out of plane and therefore deposition of C_{60} should reinforce in-plane anisotropy, which is indeed observed experimentally [11]. Finally let us note that in the case of another type of molecule more orbitals could be involved in the hybridization process which could make the general picture more complicated.

In conclusion, we have shown that a molecular C_{60} overlayer deposited on a Co thin film surface induces an out-of-plane interfacial anisotropy that is able to give birth to an inverse spin reorientation transition from in-plane to out-of-plane magnetization in the system Co/Au(111). The quantitative determination of the magnetization and anisotropy change with the C_{60} coverage compares well with *ab initio* calculations. The hybridization between C atoms and Co d_{z^2} (and, to a lesser extent, $d_{xz,yz}$) orbitals is at the origin of the reduction of the spin moment and of the local increase of the out-of-plane anisotropy. Computing the magnetic anisotropy of the surface d_{z^2} orbital for different systems, we can predict that the Fe(110) should show a decrease of PMA upon C_{60} deposition, as indeed observed experimentally. We believe that these findings are rather general and can apply to all other organic systems showing similar hybridizations.

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[1] C. Barraud *et al.*, Nat. Phys. **6**, 615 (2010).

[2] R. Lin, F. Wang, M. Wohlgenannt, C. He, X. Zhai, and Y. Suzuki, Synth. Met. **161**, 553 (2011).

[3] M. Gobbi, F. Golmar, R. Llopis, F. Casanova, and L. E. Hueso, Adv. Mater. **23**, 1609 (2011).

[4] K. V. Raman *et al.*, Nature (London) **493**, 509 (2013).

[5] Y.-J. Hsu *et al.*, J. Phys. Chem. Lett. **4**, 310 (2013).

[6] C. Vo-Van *et al.*, New J. Phys. **12**, 103040 (2010).

[7] N. Rougemaille, A. T. N'diaye, J. Coraux, C. Vo-Van, O. Fruchart, and A. K. Schmid, Appl. Phys. Lett. **101**, 142403 (2012).

[8] R. Decker, J. Brede, N. Atodiresei, V. Caciuc, S. Blügel, and R. Wiesendanger, Phys. Rev. B **87**, 041403 (2013).

[9] R. Allenspach, M. Stampanoni, and A. Bischof, Phys. Rev. Lett. **65**, 3344 (1990).

[10] G. Rodary, V. Repain, R. L. Stamps, Y. Girard, S. Rohart, A. Tejeda, and S. Rousset, Phys. Rev. B **75**, 184415 (2007).

[11] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.114.247203 for movie of the raw hysteresis cycles, x-ray magnetic circular dichroism measurements, theoretical details and results on Fe(110).

[12] E. I. Altman and R. J. Colton, Phys. Rev. B **48**, 18244 (1993).

[13] M. Callsen, V. Caciuc, N. Kiselev, N. Atodiresei, and S. Blügel, Phys. Rev. Lett. **111**, 106805 (2013).

[14] T. Moorsom *et al.*, Phys. Rev. B **90**, 125311 (2014).

[15] C. Chappert and P. Bruno, J. Appl. Phys. **64**, 5736 (1988).

[16] P. Giannozzi *et al.*, J. Phys. Condens. Matter **21**, 395502 (2009).

[17] S. L. Kawahara, J. Lagoute, V. Repain, C. Chacon, Y. Girard, S. Rousset, A. Smogunov, and C. Barreteau, Nano Lett. **12**, 4558 (2012).

[18] T. L. A. Tran, D. Çakir, P. K. J. Wong, A. B. Preobrajenski, G. Brocks, W. G. van der Wiel, and M. P. de Jong, ACS Appl. Mater. Interfaces **5**, 837 (2013).

[19] D. Li, C. Barreteau, M. R. Castell, F. Silly, and A. Smogunov, Phys. Rev. B **90**, 205409 (2014).