A nano-carbon route to rare earth free permanent magnetism

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(Dated: August 13, 2019)

Abstract

The mechanism by which paramagnetic or diamagnetic molecules are able to alter the anisotropy of transition metals remains elusive. Here, we present a molecule-metal bilayer whose low temperature coercivity of up to 1.6 T and energy product of over 350 kJ/m³ rival those of rare earth permanent magnets at low temperatures. Since this result is obtained using a non-magnetic molecule, C₆₀, such large coercivities cannot be explained by conventional exchange bias models. Instead, we propose a new form of surface anisotropy, dubbed π-anisotropy, based on the spin-dependent π-d hybridisation at metallo-molecular interfaces and the resultant spin-dependent interfacial dipole. We give evidence that this effect is currently limited to low temperatures only because of the rotational degree of freedom of the C₆₀ molecule and anticipate that further research may reveal metal-molecule composites which could exhibit this behaviour at higher temperatures.
I. INTRODUCTION

Exchange spring magnets are considered a rival to rare-earth-transition-metal (RETM) alloys for permanent magnet applications where extremely high $BH_{\text{max}}$ energy products are required. [1] Though complexes of hard and soft ferromagnets have been a subject of study for almost thirty years, concerns over supply stability of rare earths has intensified research in this area. Exchange springs comprise superlattices of alternating hard ferromagnetic films with high anisotropy and soft ferromagnets with high moment.[2, 3] The hard layers keep the soft layers pinned, meaning magnetization reversal occurs only at high fields. For transition metal/rare earth multilayers, the rare earth layer needs to be up to an order of magnitude thicker than the soft layer in order to form the appropriate microstructure. For this reason, exchange spring multilayers have struggled to challenge the impressive 380 $kJ/m^3$ energy product of NdFeB magnets. However, if the thickness of the hard ferromagnetic layer were reduced to 1-2 nm, energy products in excess of 500 $kJ/m^3$ have been predicted.[4] Here, we aim to produce this effect by using the coupling of ferromagnetic transition metals with carbon-based molecules rather than rare earths. This effectively reduces the hard ferromagnetic layer to a 1 nm hybrid interface layer, potentially providing a new route to high $BH_{\text{max}}$ permanent magnets.

The coupling between molecules and magnetic thin films has been thoroughly explored over the last fifteen years,[5] and it has been observed that anti-ferromagnetic interface states form between a variety of organic molecules and Co or Fe films, resulting in changes to the magnetic anisotropy of the system.[6–9] Furthermore, it has been observed that $C_{60}$ can have a profound effect on the band structure and magnetic behaviour of a wide range of transition metals, inducing ferromagnetic states in otherwise non-magnetic materials.[10, 11] The high electron affinity of $C_{60}$ can overcome the work function of metals such as Au, Cu and Co, leading to a transfer of spin polarised charge.[8, 12] This interfacial coupling is accompanied by the formation of a polarized $\pi$-d hybrid interface state in the $C_{60}$ band gap, leading to metallicity of the surface molecules, with a small number of available states at the Fermi energy.[13] These surface interactions result in a modified density of states (DOS) at the metal surface and the formation of an anti-ferromagnetically (AF) coupled interface state detectable by transport and spectroscopy.[8, 14] We can use these hybrid interface effects as a means to engineer and actively control the magnetic properties of metal surfaces.[15–2]
Here, we detail an exchange spring comprising a bilayer of Co/$C_{60}$ which exhibits an extremely high $BH_{\max}$ energy product at low temperatures. When the Co thin film is cubic rather than hexagonal-close-packed (HCP), Density Functional Theory (DFT) predicts the $C_{60}$ adsorption energy increases from 5.5 eV to 6.4 eV and the transferred magnetic moment increases from $1.2 \mu_B/C_{60}$ [8] to $2 \mu_B/C_{60}$, Table S1 in SI. This increase in coupling strength dramatically changes the low temperature magnetic properties of these bilayers. While Co/$C_{60}$ surfaces in general exhibit increased coercivity and decreased magnetization, cubic Co films exhibit asymmetric hysteresis loops with coercivities in excess of 1 T below 30 K, figure 1 a, b.

II. MAGNETOMETRY RESULTS

SQUID magnetometry results show that bilayers cooled in an external field appear to exhibit very strong exchange bias fields of up to 0.45 T. Exchange bias is commonly the result of coupling between ferromagnetic (FM) and antiferromagnetic (AF) layers. [18] However, in this system, there is no AF present. While the hybrid interface state exhibits anti-ferromagnetic coupling to the Co film, it has no magneto-crystalline anisotropy and is approximately 1 nm thick. Furthermore, in exchange biased FM/AF bilayers, the coercivity peaks at the Néel temperature of the AF due to its breakdown into weakly coupled grains which contribute to domain wall pinning but not to unidirectional anisotropy.[19] However, our bilayers show no such peak, implying that there is no first order transition. Analysis of the dependence of coercivity on temperature reveal two distinct regions, which can both be fit to a Jiles-Atherton (JA) model, figure 1b.[20]

The transition temperature range between these two regions corresponds closely to the range over which the rotational time-scale for a $C_{60}$ molecule is changing.[21] Below 200 K, the rate at which $C_{60}$ molecules spontaneously reorient in bulk begins to slow due to loss of thermal energy. When cooled in a saturating external field, the bilayer freezes in a configuration with very high anisotropy, with the hexagon-pentagon (h-p) of the carbon rings in $C_{60}$ in contact with the metal. This results in a spin-dependent, out-of-plane electric dipole, $\mu(S_x)$, which creates strong coupling between the in-plane spin configuration and interfacial potential. When a sufficiently large magnetic field is applied in the opposite direction, the magneto-electric torque rotates the molecules so that the nearest molecular
bond to the cobalt film becomes a hexagon-hexagon edge (h-h). The change in symmetry means the out-of-plane dipole is no longer strongly dependent on the in-plane spin configuration, reducing surface anisotropy and preventing the molecules rotating back to the h-p configuration. This irreversible rotation of the molecules means the coercivity drops by 61% after a single demagnetization cycle, figure 2 a. Changes in bias field and coercivity are commonly observed in exchange biased bilayers, a phenomenon called training that usually depends on the AF domain structure but cannot be explained in the absence of any AF order in the system. We propose that the hysteresis loops shown in figure 1a and figure 2a are not, in fact, exhibiting exchange bias but rather comprise two magnetic states, one high coercivity and one low coercivity, the former of which is destroyed by a single demagnetization cycle due to the rotation of the $C_{60}$ molecules under a magneto-electric torque. This explains the unexpected temperature dependence and magnitude of this effect both as observed in Co/$C_{60}$, and in previous studies of molecular exchange bias.

III. Π - ANISOTROPY DISCUSSION

In composites containing magnetic transition metals and light elements such as oxygen or carbon, orbital symmetry gives rise to a spin dependence in the hybridisation between p and d orbitals. Typically, this theory is applied to magnetic oxides exhibiting multiferroic effects in which the spatially anti-symmetric arrangement of oxygen ions creates a coupling between electric polarization and magnetization, but the same arguments can be applied to the interfaces between transition metals and molecules. The polarization induced by spin-dependent hybridization is defined as:

$$\vec{P} = \sum_{i,j}^{n,m} (|S_i||r_{ij}| \cos \theta_{ij})^2 \hat{r}_{ij}$$

(1)

Where $r_{ij}$ is the vector pointing from a given transition metal atom i to a light atom j with spin $S_i$. The angle between the bond and the spin is given as $\theta$. $A_{ij}$ defines the magneto-electric coupling strength. At the interface between a metal lattice comprising n bonded atoms and a molecule comprising m bonded atoms, the interfacial dipole due to spin dependent $\pi$-d hybridization is given by the sum of $P_{i,j}$ over all bonds.

If the molecule is bonded on the vertex between two hexagonal faces, the h-h orientation, all in-plane components of the polarization will cancel, leaving only the interface to break
the symmetry. Therefore, a surface dipole will only be dependent on $S_z$. However, if it is bonded between a hexagonal and pentagonal face, h-p orientation, there will be a component of $\sum S_{ij}^x \cdot r_{ij}$ which does not cancel, meaning an in-plane spin rotation will change the magnitude of the out-of-plane dipole. In addition to this spin-dependent surface dipole, there exists an in-built potential between molecule and metal.[12] The interaction between the spin-dependent dipole and in-built potential adds a new spin-dependent electrostatic term to the anisotropy of the Co surface. The irreversible breakdown of the pinning after a single sweep would then be due to a physical rotation of molecules from h-p to h-h, figure 2c. This also explains why the energy product is correlated with the rotational degree of freedom for $C_{60}$ molecules. Because this form of anisotropy arises from spin-dependent hybridization of molecular $\pi$ orbitals, we propose calling this effect $\pi$-anisotropy.

IV. TRANSPORT AND SIMULATION

The surface energy density obtained from the bias field at 3 K is 10.8 meV and the thermal energy corresponding to the centre of the transition in figure 1b is 12.8 meV. This corresponds to the energy barrier for the molecule to rotate between the h-p and h-h configuration. This energy barrier is due to the change in the surface charge dipole as the surface spins of the Co rotate, straining C-Co bonds at the surface. DFT predicts an interfacial dipole density between a 4x4 Co(111) slab and a $C_{60}$ molecule of $3.79 \times 10^{-3} \text{ e/Å}$ for the h-p configuration. The magnitude of the spin-dependent dipole is dependent on the magneto-electric coupling, $A_{ij}$, of Co/$C_{60}$, which is currently unknown. However, using example values for cobalt-ferrite gives a change in the spin dependent dipole density of $1 \times 10^{-6} \text{ e/Å}$ for a 90° rotation of the surface spins of the 4x4 Co slab.[26] This estimate assumes an average bond length of 0.14 nm and ignores any distortion of the molecule on the surface. Based on the surface dipole calculated from DFT, this gives an increase in surface energy of 20 meV during a rotation of the surface spins, making a rotation of the molecule from h-p to h-h energetically preferable. Unlike proposed mechanisms for molecular exchange bias based on conventional exchange bias theory, this model predicts an ideal surface energy density of 32 mJ/m² as compared to 0.9 mJ/m² predicted in Co/IrMn. [27] This explains how a molecule-metal bilayer is able to produce a bias field 15x greater than that observed in Co/IrMn despite the weak interactions between magnetic molecules.[19, 23] See supplemental information section
Transport measurements, micromagnetic simulations and first order reversal curve (FORC) analysis confirm this hypothesis.\textsuperscript{28} FORC analysis, shown in detail in supplemental information section S1, reveals a two-step reversal process comprising a reversible and irreversible step. The reversible step corresponds to the formation at low fields of a domain wall (DW) perpendicular to the thin film plane which is compressed toward the Co/$C_{60}$ interface. At high fields, molecules rotate, removing the surface pinning, and the vertical domain wall sweeps coherently across the film. This behaviour is also evident in the anisotropic magnetoresistance (AMR) where the DW formation at zero field can clearly be seen as a negative peak while the irreversible demagnetization at higher field does not feature in the AMR at all. After de-pinning, however, negative peaks are observed in the high field AMR for both forward and backward sweeps indicating the nucleation of domains and a radically different reversible process, figure 2a. Molecular exchange bias has previously been observed to lead to asymmetric, negative MR in thin Co films but the explanation has thus far remained elusive.\textsuperscript{29}

We performed finite-element micromagnetic simulations using Finmag \textsuperscript{30} and finite-difference simulations using Mumax3 (stable release 3.10) on a portion of a 3 nm thin Co film split into 128x128x10 cells. The Co film is given bulk values for anisotropy, $K = 60$ kJ/m$^3$, exchange stiffness, $A = 30$ pJ/m, and magnetization, $M = 1400$ emu/cc. The top surface of the Co film is in contact with an antiferromagnetic layer which simulates the surface pinning whose anisotropy barrier is $27$ MJ/m$^3$. Values were chosen to match the simulated coercivity to experimental data. The bottom surface of the Co film is in contact with a 3 nm paramagnetic layer which simulates a Ta/Co intermixing region. The hysteresis simulation is initialised in the positive x-direction and relaxed in a 2.5 T field to simulate field cooling, varying the external magnetic field between 2.5 and -2.5 T in steps of 10 mT so that half of the hysteresis loop is computed. We relax the system to an equilibrium state at each value of an external magnetic field and use the resulting configuration as an initial state for a new energy minimization. These simulations show coercivity a of 1.5 T, figure 2b. When the Co slab is saturated in the x direction, the anisotropy of the surface pinning layer is reduced to $K = 1$ MJ/m$^3$ and exchange stiffness $A = 4$ pJ/m. This simulates the depinning of the surface due to the rotation of the molecules into the symmetric h-h configuration. As a result, the sweep from -2.5 T to +2.5 T gives a coercivity of only 0.3 T.
and no vertical domain wall formation is observed.

V. STRUCTURE AND CHARACTERISATION

The cross-sectional structure of the bilayer was analysed using TEM, figure 3a. Elemental analysis showed no evidence of a CoO layer at the Co/$C_{60}$ interface. To provide proof that $C_{60}$ is responsible for these effects, a Co/$C_{60}$ bilayer was placed under a Xe-Hg arc lamp producing UV light at wavelengths of 200-400 nm for 1.5 hrs in air. UV light assists in oxidation and polymerization of the $C_{60}$ films. UV exposure was found to reduce the coercivity of the bilayer by 99% from 1.5 T to just 18 mT. Bilayer structures grown using $C_{70}$ in place of $C_{60}$ do not show the same pinning, fig 3b, even though $C_{70}$ is almost identical to $C_{60}$ in density, chemical composition and band gap, but exhibits different symmetry. TEM also showed evidence of a 1-2 nm Ta/Co interdiffusion layer, which corresponds to the paramagnetic layer in the simulations. The coercivity of these structures is highly dependent on Ta thickness, only appearing over a 1 nm window. This corroborates the prediction from DFT that the crystal structure of the Co is vital in ensuring $C_{60}$ is adsorbed in the h-p configuration, figure 3c. Further detail on the removal of $C_{60}$ using UV can be found in SI section S3.

VI. CONCLUSION

We have measured the properties of Co/$C_{60}$ bilayers which surpass all such hybrid systems observed to date and approach rare earth based permanent magnets with maximum coercivities of up to 1.6 T and $BH_{max}$ energy products of up to 356 kJ/m$^3$. We have demonstrated how these systems do not exhibit the expected behaviour of exchange bias in AFM/FM interfaces, indicating that molecular exchange bias is an entirely separate phenomenon. Non-magnetic $C_{60}$ is thus responsible for producing an exchange spring-like bilayer through $\pi$-d hybridisation at the interface producing a spin dependent surface dipole which interacts with the in-built potential to create a new form of surface or $\pi$-anisotropy. Because this phenomenon would theoretically require only a single molecular layer to pin thin metal films, bilayers of this type may represent a means to create composites with extremely high $BH_{max}$ without using rare-earths. As of yet, this phenomenon is limited to low
temperatures. However, there is evidence that the critical temperature is determined by the rotational degree of freedom of our chosen molecule, not the anisotropy mechanism. A better choice of molecule, with reduced symmetry, dopants or ligands which prevent rotation, may produce similar or even better results at higher temperatures.

VII. ACKNOWLEDGEMENTS

This work was funded by the following grants: EPSRC EP/I004483, EP/K036408, EPSRC EP/S030263/1, EP/S031081/1, EPSRC Programme grant on Skyrmionics (EP/N032128/1), The Horizon 2020 European Research Infrastructure project OpenDreamKit (676541), Taibah University PhD Scholarship. This work made use of the ARCHER (via the UKCP Consortium, EPSRC UK EP/P022189/1 and EP/P022189/1) and UK Materials and Molecular Modelling Hub (EPSRC UK EP/P020194/1) High-Performance Computing facilities.

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FIG. 1.  a. Hysteresis loop for: Ta(4 nm)/Co(3 nm)/C$_{60}$(15 nm)/Al(8 nm) after cooling down the sample to 3 K in a 2 T field, showing significantly enhanced coercivity and apparent exchange bias. The maximum coercivity, i.e the crossing point during the first demagnetization sweep, is 1.6 T. This bias disappears after a single cycle, from which we conclude that the reversal process of the Co film causes an irreversible change to the interfacial coupling between Co and C$_{60}$. Schematics show the expected molecular position after field-cooling (top) and once a large magnetic field is applied in the opposite direction (bottom). b. Dependence of the energy product of a. with temperature showing a transition between two distinct pinning regimes. This transitional range exactly corresponds to the freezing of the rotational degree of freedom in C$_{60}$. 

$E_2(0 \text{ K}) = 356 \pm 1 \text{ kJ/m}^3$

$E_1(0 \text{ K}) = 14.6 \pm 0.2 \text{ kJ/m}^3$
FIG. 2. a. Hysteresis loop for a Ta/Co/$C_60$ films. After the first demagnetization cycle, the exchange bias and pinning are irreversibly destroyed. Anisotropic magnetoresistance shows radically different reversal mechanisms in the first and second sweep. There is evidence of vertical domain wall formation around zero field (2). At the coercivity in the first sweep, there is no corresponding peak in the AMR (3 1st), indicating there is no in-plane domain wall formation. In the second sweep, peaks in the AMR are evident for both forward (3 2nd) and reverse (6) sweeps. This two-step reversal is characteristic of an exchange spring. b. Shows a hysteresis loop simulated using the Mumax3 code. The simulated Co slabs on the lower panel, extracted from the states indicated on the loop by the red arrows, demonstrate how the first sweep reversal occurs due to the formation of a vertical domain wall while the 2nd sweep reversal occurs due to lateral domain wall formation. Red regions are aligned in +x direction, blue regions are aligned in the x direction. c. Spin density at the Co-$C_60$ interface simulated via DFT. In the h-p configuration, spin density bonding is asymmetric while the h-h configuration shares symmetry with the Co surface.
FIG. 3. a. Cross section TEM of a Ta/Co/C\textsubscript{60} sample with element analysis. Notably, there is no oxygen above background noise at the Co/C\textsubscript{60} interface. This discounts the presence of thick, crystalline CoO layer which might cause exchange bias. Furthermore, there is a 1 nm diffusion layer between the Ta and Co. This layer is evident in micromagnetic simulations as a paramagnetic region on the bottom surface of the Co. This layer gives rise to the step feature at zero field in figure 1a. The presence of this layer may act to lower the barrier to vertical DW formation. b. The result of exposing a pinned Co/C\textsubscript{60} layer (black) to UV light which breaks down the molecules (blue). In addition, pinning is not obtained when using C\textsubscript{70} (red) whose density and chemistry is almost identical to C\textsubscript{60}, but has different symmetry. c. Shows the dependence of the coercivity on Ta seed layer thickness. Strong pinning only occurs in a 1 nm window of seed layer thickness.