

Tailoring the Nature of Magnetic Coupling of Fe-Porphyrin Molecules to Ferromagnetic Substrates

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We demonstrate that an antiferromagnetic coupling between paramagnetic Fe-porphyrin molecules and ultrathin Co and Ni magnetic films on Cu(100) substrates can be established by an intermediate layer of atomic oxygen. The coupling energies have been determined from the temperature dependence of x-ray magnetic circular dichroism measurements. By density functional theory + U calculations the coupling mechanism is shown to be superexchange between the Fe center of the molecules and Co surface-atoms, mediated by oxygen.

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Organic molecules as building blocks of surface-mounted nanoscale systems have gained tremendous impact in solid state physics. Besides their suitability for identical production in large quantities, molecules offer the possibility to tune relevant parameters such as surface dipolar moment [1], conductivity [2], and lateral structuring [3] by their chemical design [4]. With typical sizes of a few nanometers, they become very attractive for applications in the information technology industry [5].

Metalloporphyrins display a quasiplanar geometry, allowing for a two-dimensional assembly as electronic circuits or devices [6], while the four-ligated metal center can be accessed by two additional adsorption sites. This can be used to gain control on the metal center spin of paramagnetic porphyrin molecules. For instance, if metalloporphyrins are deposited directly on a ferromagnetic (FM) metal surface, the spin of the central ion aligns parallel to the substrate magnetization [7–9]. Very recent spin-polarized scanning tunneling microscopy studies on metallophthalocyanine molecules on Co islands reproduced the observed FM coupling [10]. Having the vision of molecular spintronics in mind, an antiferromagnetic coupling of the spin of the metal center to a ferromagnetic substrate would be a crucial step ahead. Such alignment is commonly found on transition-metal monoxides [11], where an antiferromagnetic (AFM) coupling within pairs of metal atoms is established via a superexchange interaction mediated by the oxygen. The same kind of interaction is also responsible for the ferrimagnetic ordering in single-molecule magnets [12].

In this Letter we show that an antiferromagnetic coupling between the metal center of paramagnetic Fe-octaethylporphyrin (OEP) molecules and ultrathin FM Co and Ni films can be realized by placing oxygen atoms between the molecules and the magnetic substrate. By first-

principles DFT + U calculations we demonstrate that Fe-O-Co superexchange is responsible for the antiparallel spin alignment. The strength of the AFM iron-oxygen-substrate interaction is estimated from the temperature dependence of the induced magnetization of the molecules. We find that it is comparable in magnitude to the superexchange interaction in classical transition-metal monoxide antiferromagnets [13].

Ni and Co films were epitaxially grown on a preoxidized Cu(100) single crystal, following Ref. [14]. The oxygen atoms act as a surfactant for the growth of the FM film, floating on top of the surface [14,15]. This results in a well-characterized $c(2 \times 2)$ superstructure of 0.5 ML atomic oxygen on top of the ferromagnetic films. Successively, we deposited 2,3,7,8,12,13,17,18-octaethylporphyrin-Fe (III) chloride molecules by sublimation at 490 K from a Knudsen cell onto the substrate held at room temperature. X-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) measurements were carried out by means of total electron yield detection. From an angular dependent analysis [16] of the N K edge π^* resonances, we derive a planar adsorption geometry in both cases, as shown in Fig. 3 and discussed in Ref. [8]. XMCD measurements were performed in an applied magnetic field of 20 mT along the easy axes of the Ni and Co films, i.e., the surface normal and the [110] in-plane direction, respectively. X rays with a circular polarization degree of 90% and energy resolutions set to 150 meV at the N K edge and 300 meV at the Fe, Co, and Ni $L_{2,3}$ edges were provided by the beam line UE56/2-PGM2 at BESSY. Grazing and normal incidence geometries were used with angles of $\theta = 70^\circ$ and 0° between the incoming x-ray wave vector and the surface normal, respectively. Similar spectra collected with an attenuation of the incoming beam by a factor 10 exhibited the same features for the white

lines. From this, we rule out any significant radiation-damage effects.

Figure 1 shows the Fe $L_{2,3}$ XAS and XMCD spectra for 0.6 ML Fe-OEP on O/10 ML Ni/Cu(100), O/5 ML Co/Cu(100) (red lines), and 15 ML Ni/Cu(100) (black line), measured at normal (grazing) incidence for the Ni (Co) samples at $T = 40$ K. An opposite sign of the Fe XMCD signals on the oxygen-covered Ni and Co films with respect to the substrate magnetization is observed, evidencing an antiparallel alignment of the Fe spin with the substrate. By sweeping the external magnetic field, the Fe magnetization reverses at the same field as the substrate while maintaining the antiparallel alignment. This AFM coupling is found only in the presence of the oxygen layer. In contrast, the Fe XMCD on the bare Ni film shows the same sign as the XMCD of the Ni substrate. Below we will show by DFT + U calculations that a superexchange interaction across oxygen atoms is responsible for the antiparallel alignment.

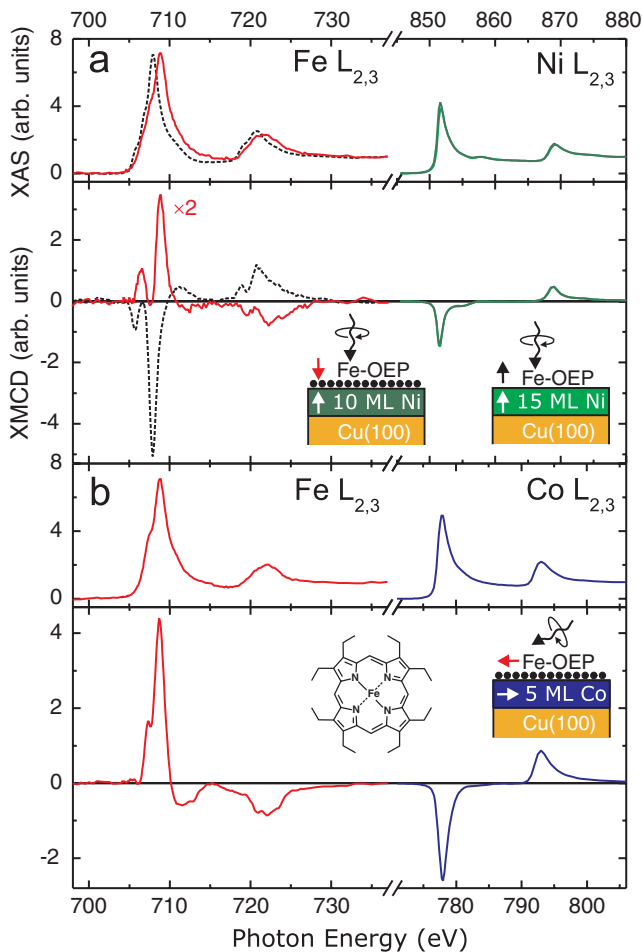


FIG. 1 (color online). Fe $L_{2,3}$ XAS and XMCD spectra of 0.6 ML Fe-OEP on O/Ni (a) and O/Co (b) (full red or gray lines), and on Ni [dashed black lines, panel (a)]. The corresponding Ni and Co spectra are shown on the right. Insets: sketches of the corresponding samples and of the Fe-porphyrin molecule.

The energy position of the Fe XAS peaks can be used as an indicator for the Fe valence state [17]. Charge-transfer processes that may occur during the evaporation and adsorption of Fe-OEP onto the O/metal substrates would affect the Fe valence state. In the case of the surfactant-grown substrates (red or gray lines in Fig. 1), the Fe L_3 XAS peak positions coincide with those of an Fe(III)-OEP-Cl bulk sample (data not shown), implying a trivalent Fe ion. On the contrary, a redshift of about 1 eV is visible on the bare metallic substrates, suggesting an increase of the number of $3d$ electrons at the Fe site.

In order to estimate the coupling energy E_{ex} of the Fe magnetic moment to the O/Ni, Ni, and O/Co substrates, we have studied the temperature dependence of the magnetizations of the FM films and of the Fe centers in the molecules. In Fig. 2 the Fe, Ni, and Co XMCD signals at fixed photon energies, normalized to the extrapolated saturation values, are plotted vs temperature. The evolution of the Fe magnetization deviates drastically from that of the substrate for all samples. For Fe-OEP on O/Co, the Fe magnetization is closer to the substrate temperature curve than for the Ni samples, indicating a stronger coupling energy. The temperature dependence of the relative Fe magnetization $M_r(T) = M(T)/M(T=0)$ has been modeled with a Brillouin function $B_J(\alpha)$ accounting for the coupling to the magnetic substrate as an effective magnetic field:

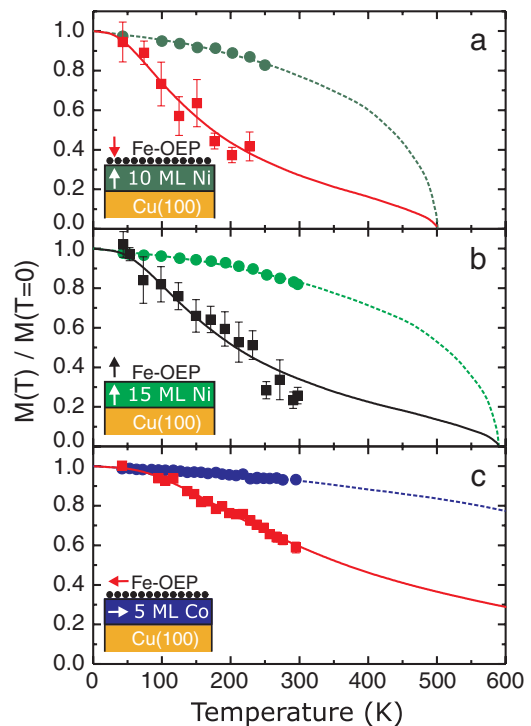


FIG. 2 (color online). Temperature dependence of Fe XMCD (squares; full lines: fit of Brillouin-type model) and Ni or Co XMCD (circles; dashed lines: empirical curve taken from Ref. [21]) for 0.6 ML Fe-OEP on (a) O/10 ML Ni/Cu(100), (b) 15 ML Ni/Cu(100), and (c) O/5 ML Co/Cu(100).

$$M_r^{\text{Fe}}(T) = M_r^{\text{sub}}(T)B_J(E_{\text{ex}}/k_B T).$$

Here we have assumed a divalent (trivalent) Fe oxidation state on the metallic (oxygen-covered) surfaces, as suggested by the XAS peak positions, and Fe intermediate spin states that result in spin moments $S = 1$ ($S = \frac{3}{2}$). By multiplying the Brillouin function with the substrate magnetization $M_r^{\text{sub}}(T)$, the thermal fluctuations in $M_r^{\text{Fe}}(T)$ are assumed to be strongly correlated to the ones of the substrates. If the spins fluctuated independently of each other, $M_r^{\text{sub}}(T)$ would enter in the argument of the Brillouin function. These two models yield very similar functional behavior and values of E_{ex} within 2%, implying that experimentally we cannot discern which model is more appropriate. However, we can assume that the Fe–substrate coupling acts on a much faster time scale than the fluctuations, consistent with the first model. For Fe-OEP on O/Co we obtain a coupling energy of 37 meV, being about half of that for the direct adsorption of the molecules on a Co substrate [9] ($E_{\text{ex}} = 70$ meV). In contrast, identical values of 17 meV are found for Fe-OEP on the oxygen-covered and bare Ni substrates. Assuming high-spin ground states, the resulting exchange energies rise by about 20% to 30%. These values are of the same order of magnitude as in transition-metal monoxides (e.g. $E_{\text{ex}}^{\text{NiO}} = 17$ meV/bond [13]).

In the following, we will discuss the role of the Fe d and N p orbitals in the magnetic coupling to the metallic and to the surfactant-grown substrates. For Fe-OEP molecules directly adsorbed onto Co metallic films, DFT + U calculations revealed a ligand-mediated indirect coupling to the substrate across the nitrogen atoms [8]. In Fig. 3 we compare the N K XAS signals of 0.6 ML Fe-OEP molecules on an oxygen-covered [panel (a)] and a bare Ni film [panel (b)]. In both cases, the spectra at grazing x-ray incidence (full lines) are dominated by two π^* resonance

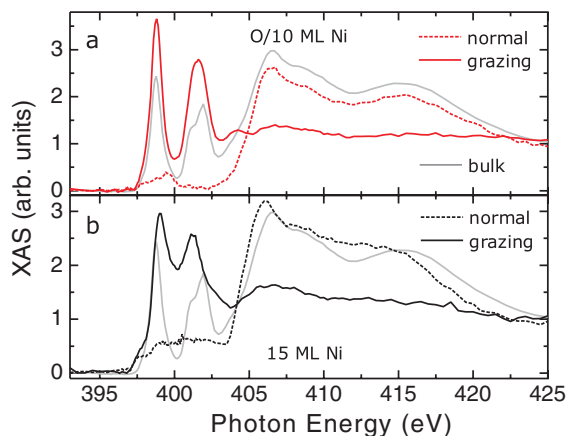


FIG. 3 (color online). N K edge XAS signals of 0.6 ML Fe-OEP (a) on O/10 ML Ni/Cu(100) and (b) on 15 ML Ni/Cu(100) at normal (dashed lines) and grazing (full lines) x-ray incidence with 0° and 70° of the E vector to the surface, respectively. The gray lines show the N K edge spectrum for a polycrystalline bulk sample.

peaks, whereas at higher energies σ^* resonance peaks appear at normal incidence (dashed lines). However, a smaller broadening and increased splitting of the N π^* resonances is observed for Fe-OEP on O/Ni, as compared to the signal on the bare Ni substrate, closely resembling the spectral shape of an Fe(III)-OEP-Cl bulk sample. This indicates an effective electronic decoupling of the N atoms from the substrate after introducing oxygen. In turn, we expect an Fe-O-Co AFM superexchange coupling that will not involve the N atoms, in contrast to the case of the metallic substrate.

For the Ni and O/Ni substrates, the measured Fe $L_{2,3}$ XMCD signals are composed of two peaks at 706.5 and 708.9 eV. In the case of the O/Co substrate, the Fe XMCD shows a peak ($E = 708.7$ eV) with a shoulder at 707.5 eV, where there is no intensity for the O/Ni sample. These different lineshapes can be understood in view of the angle dependent contributions of the individual $3d$ orbitals [18] to the total Fe XMCD signal. In systems with lower than cubic symmetry, the magnetic dipole operator contribution $\langle T_z \rangle$ cannot be neglected, leading to the strong angular dependence of the Fe XMCD signals. The XMCD signal for normal incidence, i.e., in the case of the Ni substrates, can be assigned to the in-plane d_{xy} and $d_{x^2-y^2}$ orbitals, whereas the Fe XMCD intensity on Co, measured at grazing incidence, originates from the d_{π} and d_{z^2} orbitals. They are the only ones exhibiting zero and negative XMCD intensity at normal incidence, resulting in the vanishing XMCD signal at $E = 707.5$ eV on the O/Ni substrate. The small Fe XMCD signal found on O/Ni, compared to O/Co, can be either substrate dependent or caused by the measurement geometry. The Fe XMCD signal of 0.6 ML Fe-OEP on an in-plane magnetized O/3 ML Ni/5 ML Co/Cu(100) substrate (data not shown) closely resembles the shape of the one on the O/Co surface, reduced by $\sim 30\%$. This shows that the major cause for the small XMCD in the O/Ni case is the different measurement geometry, i.e., the x-ray incidence angle, thus reflecting the influence of $\langle T_z \rangle$.

To clarify the origin of the observed magnetic interaction we performed first-principles DFT + U calculations using the full-potential, plane-wave code VASP [19]. As we showed recently, this method works well for extended magnetic systems such as metalloporphyrins on metallic substrates [8]. A 188-atom simulation cell was used, providing a good representation of the metallic substrate (3 ML). The DFT + U approach was used for the central Fe atom, with the Coulomb interaction U fixed to 4 eV and the exchange parameter J_{ex} to 1 eV. Calculations performed for freestanding porphyrin molecules proved that these values of U and J_{ex} provide the best results for both ligated and unligated Fe-porphyrin molecules [20]. The applied computational method is similar to that reported in Ref. [8], to which we refer for details.

There are several possible geometries for the Fe-porphyrin molecule, the oxygen atoms and the Co

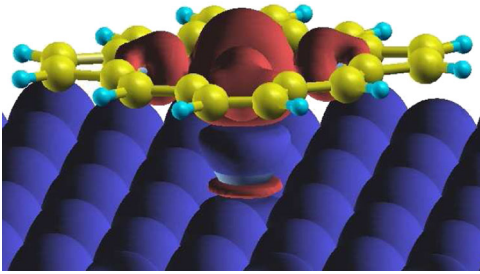


FIG. 4 (color online). *Ab initio* computed magnetization densities. Blue or dark gray color depicts majority-spin magnetization on Co atoms and on one part of the O atom, red color reveals minority-spin magnetization on the central Fe atom, on the other part of the O atom, and on the N atoms. Yellow and cyan spheres represent C and H atoms, respectively.

substrate. In one scenario, the oxygen simultaneously binds to the free ligand position of the central Fe and to a Co surface atom. Alternatively, the Fe-porphyrin molecular structure could be shifted, so that an O atom would not bind directly to the Fe. The XAS experiments indicate an Fe valency shift towards trivalent, as would be expected for Fe-O ligation. We therefore consider the first geometry in detail. This geometry can be regarded as an idealized model to elucidate the nature of the magnetic interaction, as additional oxygen atoms are not considered. We have performed a self-consistent optimization of the molecular structure, including the O ligand binding to Fe and the Co surface, by complete relaxation of the interatomic forces. Owing to the O ligation, the central Fe atom moves out of the macrocyclic plane by 0.29 Å, as typically seen for axial ligation of Fe porphyrin [20]. The computed Fe-O and Co-O bond lengths are 1.92 and 1.74 Å, respectively. These bonds are considerably shorter than the 3.4–3.5 Å Fe-Co distance computed for Fe porphyrin on Co [8], indicative of a relatively strong Fe-O and O-Co binding. The stronger binding implies that van der Waals interaction, which might be important for the molecule-surface interaction at larger distances, will not play an essential role. Our calculations yield that the O-ligated Fe-porphyrin molecule can be in a high-spin state ($4.4\mu_B$, $S \approx 5/2$) or in an intermediate-spin state ($2.9\mu_B$, $S \approx 3/2$). The high-spin state is computed to have the lowest total energy, in accordance with Hund's rule. For the computed configuration, the alignment of Fe and Co spins is always obtained to be antiparallel, irrespective of whether it is for the intermediate- or high-spin state.

To elucidate the nature of the obtained antiparallel alignment, we show the computed magnetization densities in Fig. 4. A classical picture of AFM superexchange in the Fe-O-Co path is observed: a majority-spin magnetization on Co (blue or dark gray color) couples with a minority-spin magnetization (red or gray color) of the nearest O p_z lobe, while the distant O p_z lobe has majority-spin magnetization coupled to minority-spin magnetization on the

central Fe atom. The spin magnetization densities on O are asymmetric, caused by a difference in hybridization with Co d and Fe d_π , d_{z^2} orbitals.

To conclude, we showed how to tailor the magnetic coupling between ferromagnetic Ni and Co substrates and the Fe spin at the center of porphyrin molecules. When mediated by half a monolayer of atomic oxygen, the Fe-substrate coupling is antiferromagnetic. This situation is in contrast to the previously found ferromagnetic coupling of Fe-porphyrin molecules directly adsorbed onto the magnetic substrates. Our DFT + U calculations showed that the responsible coupling mechanism is antiferromagnetic superexchange mediated by the oxygen p_z orbitals. The corresponding coupling energies have been obtained from the temperature dependence of the Fe and substrate magnetic moments. This study unveils completely new possibilities to realize the vision of a molecular spintronic device in which a spin-polarized current can be used to switch the metal-ion spin from antiparallel to parallel alignment respective to the substrate magnetization, which cannot easily be achieved for ferromagnetic coupling.

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