Iron Phthalocyanine and ferromagnetic thin films: magnetic behavior of single and double interfaces

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Co film growth on Cu(001) and Cu(111) surfaces

Bulk Co presents fcc structure for T>710K and hcp structure for lower temperature. Due to the small mismatch between the lattice parameter of Co on Cu surface it is possible to grow Co film with fcc or pseudo fcc structure even at room temperature (RT). The magnetic properties, such as coercive field, Curie temperature and magnetic anisotropy, depend on the Co film thickness and deposition conditions. Co thin film grown on Cu surfaces shows characteristic structural and magnetic phase transitions as a function of film thickness (t). The onset of structural and magnetic transition differs for each Cu surface.¹² Co film has pseudo fcc structure as grown on Cu(001) and fcc on Cu(111)) surface for t ~ 6ML (~1.1 nm) and t ≤ 2ML (~0.5 nm) respectively, and in-plane easy magnetization axis.¹² We prepared two thin films of 0.5 nm on Cu(111) and 1.4 nm on Cu(001), both of them are expected to
grow in fcc or pseudo-fcc structure and with magnetization in the surface plane and a Curie temperature above RT. The roughness of Co film may affect the growth of FePc film and the magnetic coupling between the molecules and the underneath substrate.³

**Experimental geometries**

![Experimental geometries](image)

Figure S1: (a) The experimental geometry of X-ray linear dichroism, XLD: X-ray linear polarized beam impinges on the sample at $\theta = 60^\circ$ (grazing) and $\theta = 0^\circ$ (normal incidence). (b) XPS experimental geometries: the angle between X-ray linear polarized beam and the analyzer axis is $\theta = 45^\circ$. The measurements were performed at $\theta = 45^\circ$ (normal emission, NE) and $\theta = 0^\circ$ (45°) off NE.

The ordering of the molecular film grown on metallic substrate is studied by using the search light effect, i.e. different selective absorption of in–plane and out–of–plane molecular
Figure S2: (a) XMCD at APE: the measurements are performed on samples in remanent magnetization by reversing the photon helicity. The magnetic field is applied along the sample surface and with an angle between photon beam and sample normal of $\theta = 45^\circ$. (b)-(c) XMCD and hysteresis loop at DEIMOS: the measurements are performed with a magnetic field of 6 T applied at angle of $\theta = 60^\circ$, $30^\circ$, $0^\circ$ with respect to the sample normal. (d) remanent XMCD, DEIMOS: a magnetic field of 6 T is applied along the sample surface and XMCD spectra measured $\theta = 60^\circ$.

orbital when excited with linear polarized light. Figure S1 display the experimental geometry for X-ray linear dichroism measurements, where the light polarization is along or almost perpendicular to the substrate surface. The growth of the Ni overlayer on the molecular film was monitored by measuring X-ray photoemission spectra as a function of Ni thickness and the angle between the sample normal and analyzer axis. XPS experimental geometry is illustrated in panel (b) of Figure S1. The characterization vs Ni thickness allows us to discern in the spectra the evolution of features related to the chemical interaction between Ni atoms and the molecular film. On the other hand, XPS measurements as a function of angle gives information about C 1s and N 1s environment at different depth(normal emission, more bulk sensitive, whereas 45 off normal emission is more surface sensitive) within the molecular film.
The magnetic properties of the metallic ferromagnetic and of the molecular films are measured by XMCD. Different XMCD experimental geometry are used in APE and DEIMOS. At APE an in–situ electromagnet applies a pulsed magnetic field up to ±0.05 T along one direction in the sample surface plane (Figure S2 (a)). XMCD spectra are measured on samples in remanent magnetization by reversing the photon helicity. At DEIMOS, XMCD measurements have been carried out in total electron yield mode at ∼4 K with a magnetic field of 6 T parallel to the X-ray propagation direction. The measurements were performed at different angles (0 °, 30°, 60°) with respect to the surface normal (Figure S2 (b)-(c)). Some of the XMCD measurements were performed in remanence (after applied a magnetic field of 6T) with magnetization aligned along the sample surface and by reversing the light polarization (Figure S2 (d)).

**Calibration of the evaporation sources**

We performed the calibration of Ni thickness by measuring XPS on Ni thin film deposited on Cu(001) surface. Core level intensity is proportional through a constant to photoemission cross section (σ), inelastic mean free path (λ), number density and the detection angle (θ) with respect to the sample normal. The most common approach to determine overlayer thicknesses assumes that an increasing overlayer thickness causes an exponential attenuation of the photoelectron signal. In the case of Ni film of thickness t, the attenuation through of photoelectron intensity is given by:

\[ I_{Ni} = I_{Ni0} \sigma_{Ni}(1 - e^{-t_{Ni}/\lambda_{Ni}(E_k(Ni))}) \] (1)

whereas the intensity from the Cu is given by:

\[ I_{Cu} = I_{Cu0} \sigma_{Cu}(1 - e^{-t_{Ni}/\lambda_{Ni}(E_k(Cu))}) \] (2)
Figure S3: Cu $3p$ core level photoemission spectra before and after the deposition of nickel film.

In the case of normal emission experiment and elements that are close in kinetic energy the two equations above can be simplified and the thickness of the overlayer can be calculated as:

$$t_{Ni} = \frac{\lambda_{Ni}}{I_{Cu} \sigma_{Ni}} \ln(1 + \frac{I_{Ni} \sigma_{Cu}}{I_{Cu} \sigma_{Ni}})$$

with $\lambda_{Ni} = 0.588$ nm at $\sim 400$ eV and gives $t_{Ni} = 0.5$ nm.

The thickness of cobalt and nickel films were determined at DEIMOS beamline by using a previous calibration of Co and Ni XAS spectra with the microbalance deposition rate.

**FePc film growth on Co film**

$45^\circ$ ($60^\circ$) at APE (DEIMOS) as shown in Figure S4. Absorption is promoted within unoccupied orbitals that are spatially oriented parallel to the electric field. FePc molecules are,
Figure S4: (a) N K XAS spectra of FePc film grown on Cu(001)/Co(1.4nm)/FePc(3nm) at APE; (b) Fe L$_{2,3}$ XAS spectra of FePc film grown on Cu(001)/Co(1.4nm)/FePc(3nm) at APE (bottom) and of Cu(111)/Co(0.5nm)/FePc(1nm) prepared at DEIMOS.

...to first approximation two-dimensional. The unoccupied $\sigma^*$ ($\pi^*$) orbitals of the nitrogen sites in FePc are directed in (out of) the molecular plane. If the molecules have the same orientation, the orbital anisotropy can be maintained and revealed by XLD. Thus, in our experimental geometry, the molecules lying flat on the underlying substrate should lead to a higher X-ray linear dichroism, i.e. the efficiency of the transition into $\pi^*$ ($\sigma^*$) unoccupied state for X-ray linear horizontal polarization. Figure S4 (a) displays an almost null XLD at N K and Fe L edges of FePc film grown on Cu(001)/Co(1.4nm) substrate, i.e. the molecules are randomly distributed in the FePc multilayer. On the other hand, Fe L$_{2,3}$ XAS spectra of Cu(111)/Co(0.5nm)/FePc(1nm) show a clear XLD (the upper panel of Figure S4 (b)) signature of a ordered film growth. The observed FePc film organization on Co surfaces may be due to the use of different Cu substrates and their roughness that may change in...
time as a consequence of several sputtering and annealing cycles. It has been demonstrated that Co film roughness may affect the molecular film growth.$^3$

**Ni growth on FePc film**

The thin film formation on a crystalline substrate follows different routes: layer-by-layer (1), island-like (2) and layer plus island (3) depending on whether the interaction between the substrate and the film is stronger (1) than the one between neighbouring atoms (2) or intermediate (3). At each film growth corresponds an interface, i.e. the contact region between two materials that present concentrations gradually changing with distance (grade interface) or an abrupt change in concentration (sharp interface). If one of the materials is a molecular film its roughness and the vacancy within it may favor diffusion of the metal layer as well as chemical interaction with it.

Figure S5 shows the profile of ordered (a) and disordered (b) FePc film with a roughness of the order of 0.15 and 1.5 nm respectively. The growth of metal film on rough surface implies the presence of the metal atoms at different height with respect to film surface.

According to the correlation between the metal film formation and the ionization potential established in Ref.$^6$ the metals with low ionization potential are easily ionized and enter in the molecular matrix, whereas metal with higher ionization potential remain neutral at the surface of the film and form clusters. Ni has an ionization potential of 7.64 eV higher than In but smaller than noble metal, and an atomic radius of 0.163 nm, therefore is expected to give low diffusion and metal film growth on top of the molecular film.

Here, we concentrate in explaining our understanding of how Ni film grows on top of the molecular film using the evolution of intensity and spectral shape of XAS and core level photoemission spectra. In Figure S6 we show Ni and Fe $L_{2,3}$ XAS spectra and their intensity as a function of metal overlayer thickness. Fe XAS spectra undergo to a lineshape and intensity modification; whereas Ni spectra present typical features of metallic film, i.e. $\frac{L_3}{L_2}$
ratio $\sim 3$ and the shoulder at 6 eV above the L$_3$ edge. Fe electronic configuration broadens and the low photon energy feature of Fe L$_3$ XAS drops in intensity when Fe atoms are in contact with Ni atoms. We observed in$^7$ that the intensity attenuation of Fe XAS intensity as a function of Ni film thickness decreases following exponential decay $exp(-d/k).$ This is consistent with a homogeneous metal coverage on top of FePc.

We monitored the evolution of C $1s$, N $1s$ and Ni $3p$ core level photoemission spectra as a function of Ni thickness. An intensity decrease of C $1s$ and N $1s$ spectra is observed as well as a modification of their lineshape upon Ni deposition, whereas Ni $3p$ core level peak increases in intensity and does not vary its profile. C $1s$ and N $1s$ intensity decrease is due to the attenuation through the Ni thin film. 480 eV is favorable photon energy for measuring.
Figure S6: Ni (a) and Fe (b) L\textsubscript{2,3} edges XAS spectra measured as a function of Ni thickness. (c) Fe and Ni XAS intensity vs Ni thickness. A guide line is used to connect the point.

Table S1: Photo-ionization cross section in MBarns (Ref.\textsuperscript{8}) of the atomic orbital of FePc, Co, Ni

| element | orbital | \(\sigma(480\text{eV})\) |
|---------|---------|-----------------|
| N       | 1s      | 0.47            |
| N       | 2s      | 0.0208          |
| N       | 2p      | 0.0045          |
| C       | 1s      | 0.2989          |
| C       | 2p      | 0.0012          |
| Fe      | 3d      | 0.1085          |
| Co      | 3d      | 0.1592          |
| Ni      | 3d      | 0.2258          |
| Ni      | 3p      | 0.326           |

C 1s and N 1s core-level since their photo-ionization cross sections are 0.47 and 0.3 MBarns (Table S1) and the electron effective attenuation length at kinetic energy of 200 eV (C 1s) and 78 eV (N 1s) is of the order of \(\sim 0.3\) nm and corresponds to an overall probing depth of \(\sim 1\) nm (\(\sim 0.6\) nm). On the other hand, at 480 eV the measurement of FePc valence band (mainly N 2p, C 2p and Fe 3d) is feasible only on pristine film, but difficult after Ni deposition since N 2p and C 2p photo-ionization cross-sections are two orders of magnitude smaller than Ni 3d.

We evaluated roughly the amount of Ni atoms deposited on the molecular film through
Figure S7: The fitting of C 1s XPS measured at (a) NE emission and (b) 45° off NE, (c) Ni 3p core level spectra as a function of Ni thickness; (d) the ratio of $\frac{C_{-Ni}}{C_{1s}}$ (left axis) and $\frac{C_{-Ni}}{Ni_{3p}}$ vs. Ni thickness.

In Figure S7 we reported C 1s XPS spectra measured at NE (a) and 45° off NE (b) and their decompositions into: features related to C atoms in benzene ($C_B$) and pyrrole ($C_{Pyr}$) macrocycle and their shake-up satellites, vibrational and C-Ni peaks. We measured C 1s and N 1s XPS spectra in two geometries: normal emission (sensitive to deeper region of the sample) and 45° off NE (surface sensitive). The most intense C-Ni and N-Ni signals are detected in normal emission geometry. The roughness of the molecular film or Ni diffusion within the molecular film may cause the localization of Ni atoms at different depth with respect to the Ni surface. In broaden interface the normal emission spectrum provides contributions relative to Ni at different distance with respect to film surface. We evaluated the ratios $\frac{C_{-Ni}}{Ni_{3p}}$ and $\frac{C_{-Ni}}{C_{1s}}$ that give the percentage of Ni atoms interacting with C and the number of C atoms bounded with Ni. Both ratios are corrected by photoemission cross-section of C 1s and Ni 3p at 480 eV as reported in TableS1. $\frac{C_{-Ni}}{Ni_{3p}}$ decreases as a function of Ni thickness, while $\frac{C_{-Ni}}{C_{1s}}$ increases by increasing Ni content. This can be explained in terms of different effects: (i) 50 % of Ni interacting with C are at different depth with

the area within Ni 3p peak after background substraction. Some Ni atoms are in contact with molecular film and interact with them as shown by the modification of C 1s and N 1s lineshape, i.e. C-Ni (N-Ni) features at low binding energy in the photoemission spectra. In Figure S7 we reported C 1s XPS spectra measured at NE (a) and 45° off NE (b) and their decompositions into: features related to C atoms in benzene ($C_B$) and pyrrole ($C_{Pyr}$) macrocycle and their shake-up satellites, vibrational and C-Ni peaks. We measured C 1s and N 1s XPS spectra in two geometries: normal emission (sensitive to deeper region of the sample) and 45° off NE (surface sensitive). The most intense C-Ni and N-Ni signals are detected in normal emission geometry. The roughness of the molecular film or Ni diffusion within the molecular film may cause the localization of Ni atoms at different depth with respect to the Ni surface. In broaden interface the normal emission spectrum provides contributions relative to Ni at different distance with respect to film surface. We evaluated the ratios $\frac{C_{-Ni}}{Ni_{3p}}$ and $\frac{C_{-Ni}}{C_{1s}}$ that give the percentage of Ni atoms interacting with C and the number of C atoms bounded with Ni. Both ratios are corrected by photoemission cross-section of C 1s and Ni 3p at 480 eV as reported in TableS1. $\frac{C_{-Ni}}{Ni_{3p}}$ decreases as a function of Ni thickness, while $\frac{C_{-Ni}}{C_{1s}}$ increases by increasing Ni content. This can be explained in terms of different effects: (i) 50 % of Ni interacting with C are at different depth with
respect to Ni film surface as indicated by a ratio \( \frac{C-Ni(NE)}{C-Ni(45^\circ \text{off NE})} \); (ii) the intensity of core level spectra relative to C atoms far from the interface are more attenuated by increasing the Ni content. Upon Ni deposition on FePc we observed an initial rapidly decrease in C 1s and N 1s intensity and a metallic like Ni 3p features supporting limited diffusion and metal film formation.

Ni deposition on ordered and disordered FePc film

Figure S8: N K XAS spectra of FePc film grown on Cu(111) (a) and Co(1.4nm)/Cu(001) (b) surfaces and acquired at grazing \( \theta = 60^\circ \) (45°) and normal incidence \( \theta =0^\circ \). N 1s (c) and C 1s (d) XPS spectra measured on Cu(111)/FePc(3nm) and on Cu(001)/Co(1.4nm)/FePc(3nm)/Ni(4nm) at 480 eV as function of the angle between sample normal and detector axis.(e)-(f) schematics of FePc film organization and Ni adsorption on the molecular film on Cu(111) and Cu(001)/Co(1.4nm) surfaces.

To determine whether the ordering of the molecular film may affect the growth of the top Ni film we prepared two samples: FePc(3nm)/Co(1.4nm)/Cu(001) and FePc(3nm)/Cu(111) in the same experimental facility, APE. Since we used the same preparation instruments and conditions, the thickness calibration and the sample recipies are well defined. N K XAS spectra of FePc(3nm)/Cu(111) and FePc(3nm)/Co(1.4nm)/Cu(001) correspond to a
well ordered (Figure S8 (a)) and disordered FePc film (Figure S8 (b)). We measured X-ray photoemission spectra at 480 eV in two geometries: one more surface sensitive (the angle $\theta$ between the sample normal and analyzer axis is 45 °) and one more bulk sensitive ($\theta = 0 ^\circ$, normal emission). In both cases we can observe that the spectral feature attributed to the bonding of Ni atom with C and N atoms is more intense in normal emission geometry, despite the different roughness of molecular film (Figure S8 (e) and (f)).

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