

The Formation of Metallic Ferromagnetic Thin Film on Top of an FePc Ordered Thin Film: The Chemical and Magnetic Properties of the Interface

Emilia Annese,^{*,†} Giovanni Di Santo,[‡] Fadi Choueikani,[¶] Edwige Otero,[¶] and
Philippe Ohresser[¶]

[†]*Centro Brasileiro de Pesquisas Físicas, Rio de Janeiro 22290-180, Brazil, and Elettra
Sincrotrone Trieste, s.s. 14km 163.5, 34149 Trieste, Italy*

[‡]*ST-INSTM laboratory, Elettra Sincrotrone Trieste, s.s. 14km 163.5, 34149 Trieste, Italy*

[¶]*Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP48, 91192 Gif-sur-Yvette,
France*

E-mail: emiliaannese@gmail.com

Ni(y)/Cu(100) and onset of in-plane magnetization

Figure S1 shows Ni $3p$ and Cu $3p$ before and after Ni deposition of 0.5 nm. In correspondence of this thickness we do not observe the substrate signal in the photoemission spectrum and we measured the Ni XMCD signal of 15% for magnetization alignment along the sample surface. We report these data as a term of comparison with respect to Ni film on top of molecular film.

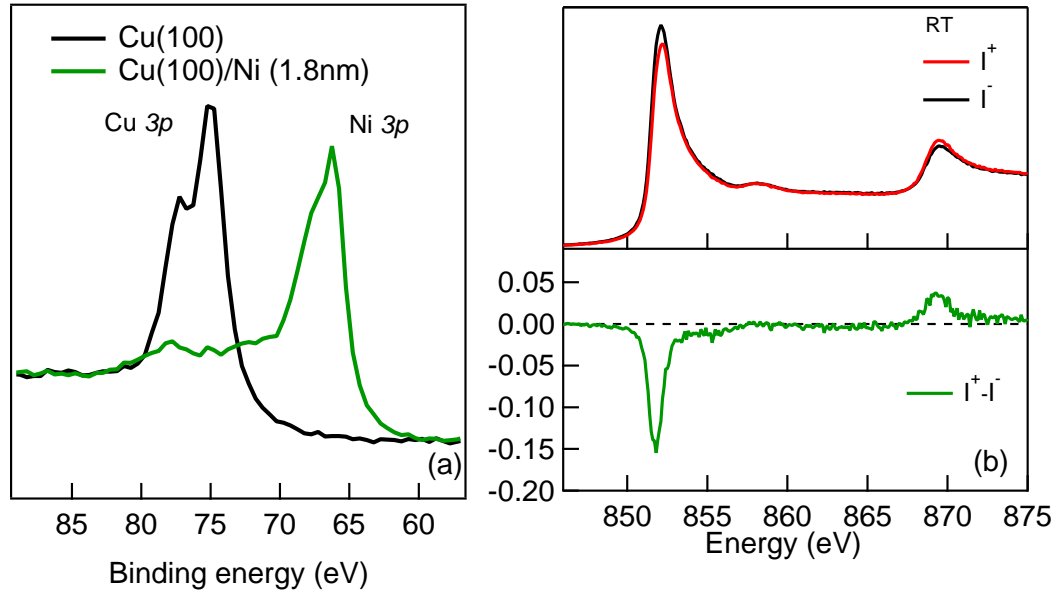


Figure S1: Ni $3p$ core level spectra and Ni (b) $L_{2,3}$ edges XAS spectra measured by varying photon helicity at remanence and at $\theta = 45^\circ$.

N K and Fe $L_{2,3}$ XAS intensity vs Ni and Co overlayer thickness

Figure S2 shows N K (a) and Fe L_3 (b) and Ni $L_{2,3}$ (c) XAS spectra measured of the same sample after subsequent Ni deposition. It is possible to follow the XAS intensity variation: the one relative to the molecular film (N, Fe) decreases upon Ni content increases. XAS spectra were normalized to the synchrotron ring current. Similar behavior was observed

for N and Fe XAS spectra (the line shape different due to selectivity of light search effect) measured on the sample at $\theta = 0^\circ$. According to this normalization it is not easy to observe the spectral line shape modification, therefore in the main text of the manuscript we normalized to 1 the maximum spectral intensity.

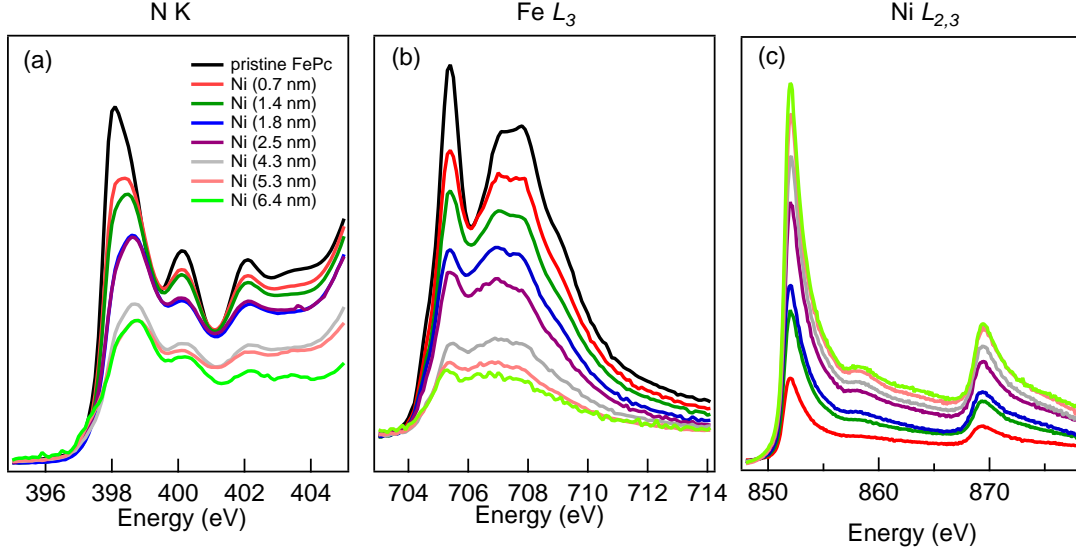


Figure S2: N K (a), Fe L_3 (b) and Ni (c) $L_{2,3}$ edges XAS spectra measured as a function of Ni thickness at $\theta = 45^\circ$.

Figure S3 shows N K (a) and Fe L_3 (b) XAS data measured of the same sample after subsequent Co deposition. It is possible to follow the XAS intensity variation: the one relative to the molecular film (N, Fe) decreases after first Co deposition and no big intensity variation was determined for the subsequent Co evaporations. Similar behavior was observed for spectral XAS intensity measured on the sample at $\theta = 0^\circ$. We repeated Fe L_3 XAS measurements (c) on the FePc(1.5 nm)/Cu before and after Co deposition, on the sample used for the XMCD measurements in remanence and applied magnetic field. An evident quenching of the low energy feature of Fe XAS indicated the involvement of Fe 3d out of plane orbital in the interaction with Co top layer.

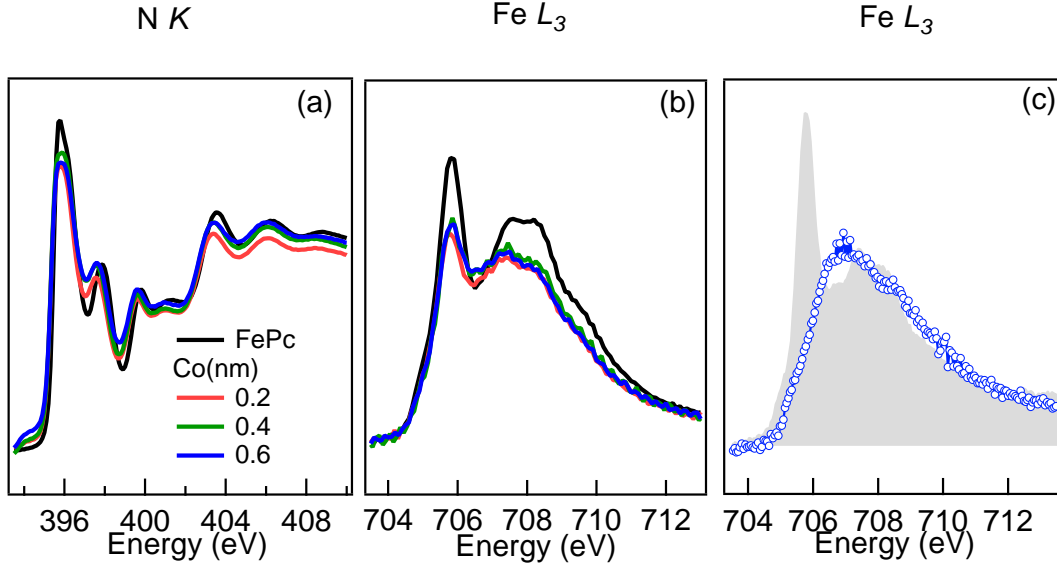


Figure S3: N K (a), Fe L_3 (b-c) edges XAS spectra measured as a function of Co thickness at $\theta = 45^\circ$ (panel c at $\theta = 60^\circ$). Panel (c) shows Fe L_3 XAS measured on the same sample used for the XMCD measurements with and without magnetic field.

C $1s$ and N $1s$ core levels vs Ni and Co thickness and experimental geometry

Photoelectron spectroscopy (PES) probing depth depends on the experimental geometry. In the most common one electrons are acquired along the sample surface normal, i.e. normal emission (NE) geometry. However, the surface sensitivity is enhanced by measuring at take off angle with respect to NE. Figure S4 (a) illustrates the variation of electron probing depth at different experimental geometries. Moreover, the overall intensity of the PE spectra varies in terms of the relative angle between sample normal and X-ray beam along with the footprint of latter.

PES is sensitive to symmetry of the orbital involved in the process as well as atom environment. Electron state symmetry can be determined by using linear s-(-p)polarized X-ray beam and varying its relative position with respect to and sample surface. Figure S4 (b-c) shows the selectivity of odd(even) orbital symmetry by using s-(-p) polarized X-

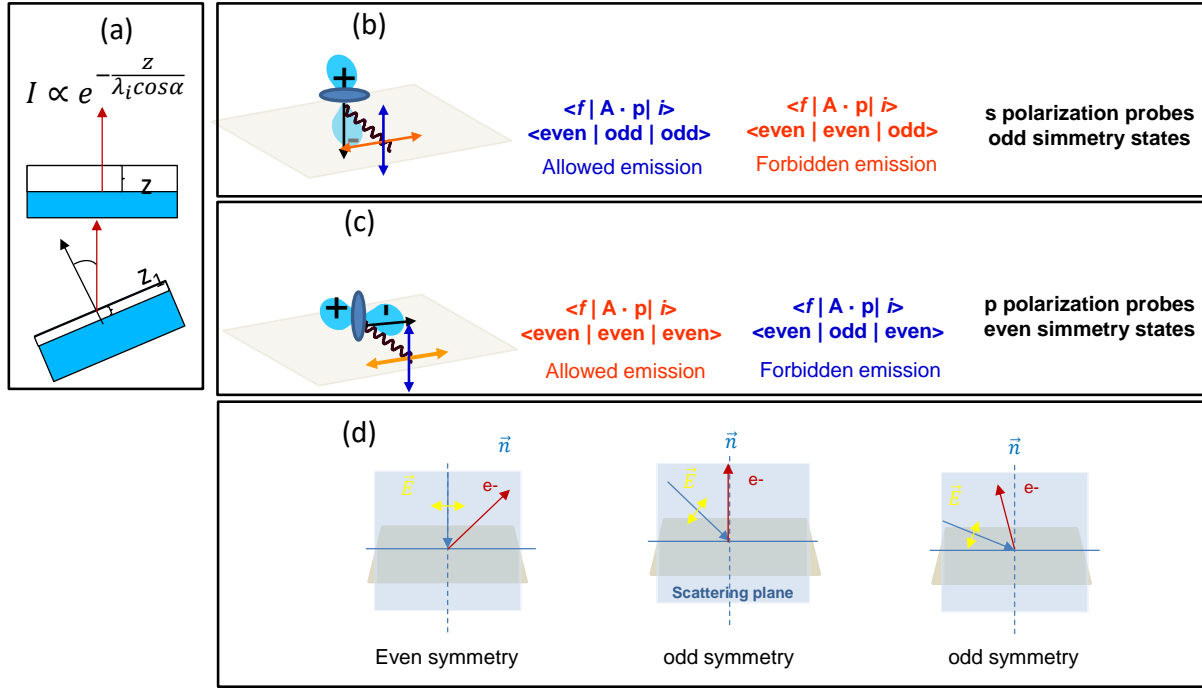


Figure S4: (a) A scheme that explains the mean electron probing depth (MEPD) dependence on the experimental geometry: at fixed kinetic energy of photoemitted electron MEPD is smaller at higher take off angle from surface normal. Orbital symmetry determination by photoemission polarization selection rules: s(-p)polarized light selects odd (even) states (b,c) with respect to the plane perpendicular to the scattering plane. (d) Drawing of the photoelectron experiment geometries: light polarization and electron directions are highlighted as well as the most probable orbital symmetry to be probed. The incident X-ray beam and detected electrons are in the scattering plane.

ray. Figure S4 (d) illustrates the experimental geometries used in this work and the most probable orbital symmetry to be probed for each one.

Figure S5 shows representative C $1s$ and N $1s$ PES data for pristine FePc film and Ni atop film of thickness 4 and 6 nm at 480 eV and at $\alpha = -45, 0, 15^\circ$. All the spectra were normalized to the maximum spectral feature to highlight the line shape variation. Before normalization, the overall spectral intensity was maximum in the geometry at 15° corresponding to the

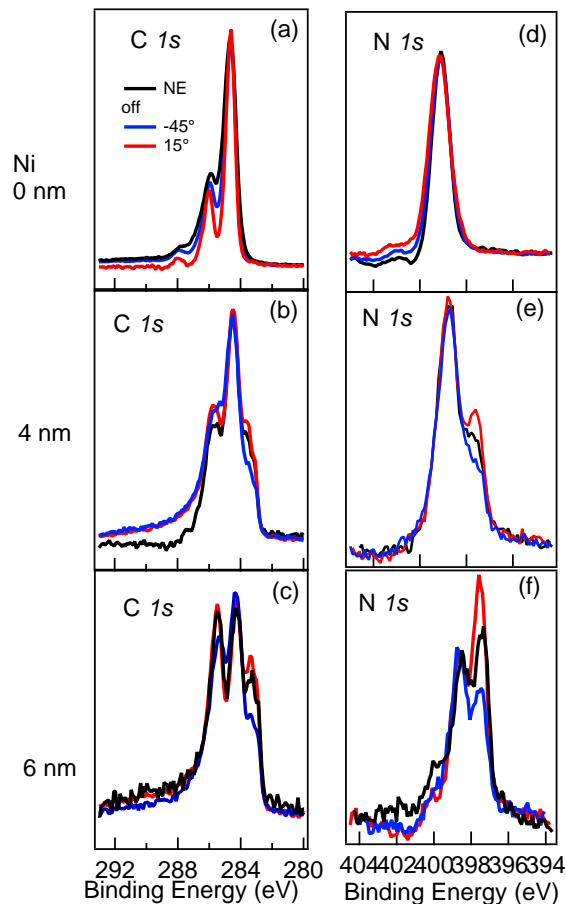


Figure S5: C $1s$ (a-c) and N $1s$ (d-f) XPS measured at normal emission, NE, (black), and at take off angle from NE 15 ° (blue) and (b) -45 ° (red). The spectra are shown for pristine and selected thickness: 4 and 6 nm.

biggest X-ray footprint on the sample surface.

Panel (a-d) of Figure S5 displays the C $1s$ and N $1s$ spectra of pristine FePc film vs α . No significant line shape change was observed for FePc film before Ni deposition. Upon Ni adsorption on FePc film, we observe extra features, C-Ni_x and N-Ni_x (as explained in the manuscript), at low binding energy side for both C $1s$ and N $1s$ spectra. C-Ni_x and N-Ni_x intensity is maximum at take off angle of 15 ° and minimum at -45 °. This behavior cannot be explain only in terms of MEPD, since in this case an intensity increase of C-Ni and N-Ni would be expected from 15 ° to -45 °. Core level measurements were performed with linear X-ray and photoemission and varying the relative position of electric field and

surface normal, which corresponds to activate selection rule sensitive to the symmetry of the orbital involved in the spectral feature. An increase of C-Ni_x and N-Ni_x intensity going from NE to -15 ° suggests an even symmetry with respect to the scattering plane. We attributed C-Ni_x and N-Ni_x as originating from Ni 3d_{z²} bounding with C and N atoms.