ESRF	**Experiment title: Magnetic characterization of guest atom clusters templated by an extended, highly regular metalorganic coordination network**	**Experiment number**:
Beamline:	**Date of experiment**: HC-3010 from: 29/06/2017 to: 11/07/2017	**Date of report**: 8/09/2017
Shifts:	**Local contact(s)**: Emilio Velez-Fort and Nicholas Brooks	*Received at ESRF:*

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Experimental Report:

General evaluation of the beamtime

Despite the loss of half of the beamtime, we are quite satisfied by the outcome of this experimental run and the support received by the local staff. The measurements that we carried out in the first three days point towards very interesting results that must be analysed in depth. The loss of three days of our experiment was due to the break down of the transfer arm on the distribution chamber. As this prevented any substrate exchange, we could not produce new samples and that inhibited us from producing the required data to fulfill the proposal goals.

Carried measurements and sample preparations

The measurements that were carried out have been mainly centered in the measurement of linear and circular dichroism at normal (0º) and grazing (70º) incidence as function of the magnetic field. This allowed us not only to measure single dichroic spectra (with linear and circular polarization), but also histeresys loops. Each sample measured took close to a day because the signal of interest came from the suface and the amount of material is rather small (only a few tenths of a monolayer) yielded tiny signals over large bulk backgrounds. In particular, we recorded every spectra several times (generally 8 times per light polarization and magnetic field applied).

Given the long acquisition times and in order to reduce dead times by sample preparation and sample exchange, we worked with three different substrates: flat-Cu(111), curved Cu(111) and flat-Au(111). The preparations were carried out while another sample was measured, which put considerable pressure on the team. Moreover, to have a reference of every system, the evaporation of the molecules (DCA) was done using a mask, so that only a part of the sample was covered by the network. This saved a lot of time since the coverages of the transition metals was exactly the same with or without the presence of the molecular network.

The samples that we measured (in chronological order) were the following:

i) Fe (nanodots)/DCA/flat-Cu(111). The Fe was deposited with the substrate at RT.

ii) DCA/curved-Cu(111). Step density changing with position. Network covering half of the sample.

iii) Fe (nanodots)/DCA/flat-Cu(111). The Fe was deposited with the substrate at LT (110 K).

iv) Co/DCA/Au(111). DCA network having Co atoms as ligands. Imperfect sample.

Results from this beamtime

Our major concern was to check if there was any beam damage over the molecular porous network. We did many test using samples i) and ii), but found no modification of the absorption spectra over Fe or Cu.

Note that we also attempted to determine the contribution of the N atoms (located at the cyano groups of the molecules) to the DCA, but the N K-edge signal was far too low due to a poor transmission of the incoming light at these photon energies and no sound data has been taken. Even so, for precaution we changed the position of the beam after roughly 2 hours.

Our first goal was to determine if Cu coordination atoms did show any magnetic moment or anisotropy when embedded in a network. For that we measured sample ii), but our quick pre-analysis does not show any hint in this respect. The background masks any possible weak feature stemming from the coordinating atoms. We also looked at the case of N atoms to the coordination atoms, but likewise the signals are too small to detect.

The second goal was to study the magnetic fingerprints of Fe clusters when the molecular network was present on the surface. Samples i) and iii) were measured for this purpose and the results are really promissing. Indeed, the molecular network breaks up the Fe into small clusters of the order of 2 to 5 nm^2 in area, featuring hysteresis loops with a larger coercivity, probably due to an enhanced anisotropy (as shown in Fig. 1). The comparison to the same Fe coverage grown directly on Cu(111) leaves no doubt about it.

Furthermore, based on our previous home-lab STM experiments, samples i) and iii) present different nanodot sizes, which are generated by changing the substrate's temperature while depositing Fe. We observe differences in the collected data but a more thorough analysis is required to reach a conclusion.

Sample iv) was measured just before the transfer chamber failure. The preparation sample had been imperfect (cf. STM image of Fig. 2) as there are scarce Co islands coexisting with the Co coordinated network (the Au substrate does not generate the porous network by itself). The hysteresis loops show openings and closing close to zero field, but we need to investigate this further since the shape and magnitude could be altered by the presence of Co clusters.

Outlook

Due to the loss of 3 days of beamtime we could not accomplish all the goals of this proposal. For instance, we could not find out the characteristic temperatures for the Fe clusters or perform experiments adsorbing oxigen. Conversely, we have found very intriguing magnetic signals when the DCA network uses Co atoms for coordination of the DCA molecules. Thus, we plan to do a follow up of these measurements in a future beamtime.

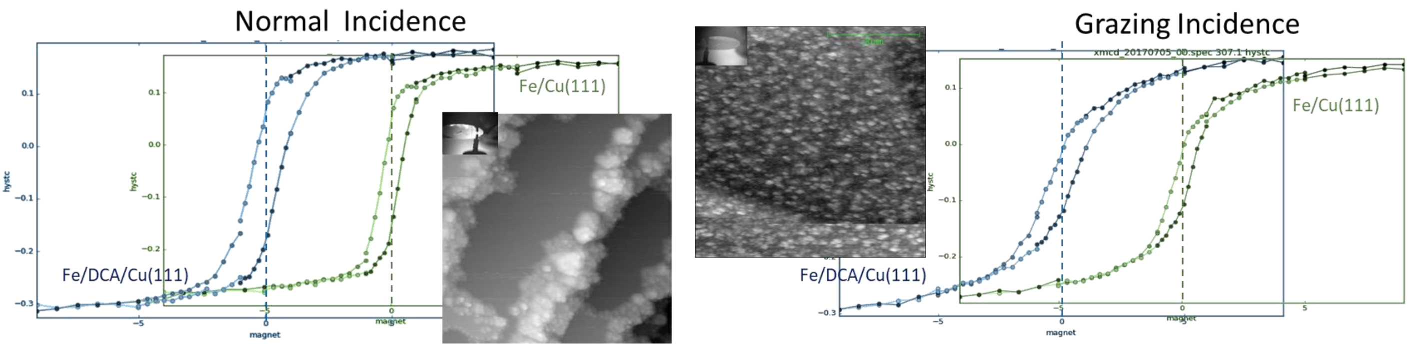

Figure 1. *Measured hysteresis loops at normal incidence and grazing incidence for Fe clusters on top of the DCA network (blue lines) and Fe islands on Cu(111) (green lines). The hysteresis of Fe/Cu(111) is horizontally shifted (maintaining the scale) for better visualization. Even if the Fe coverage is equal for both, the morphology is different, as shown in the STM pictures (acquired during this beamtime).*

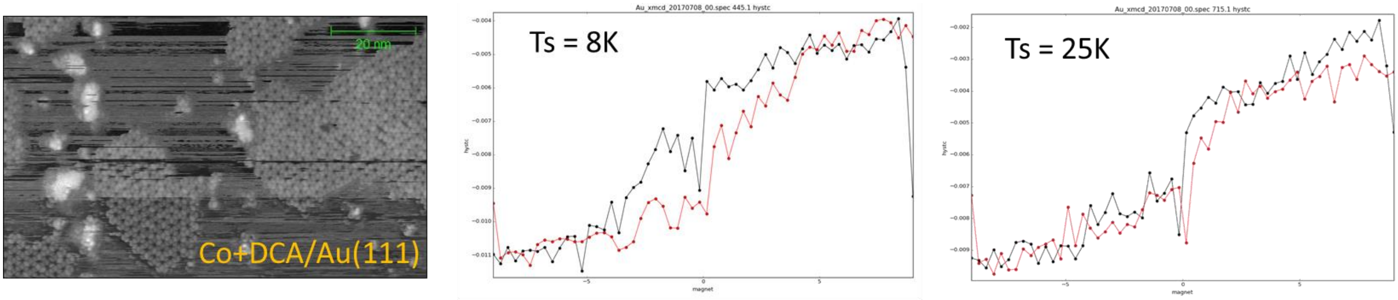

Figure 2. *STM image and measured hysteresis loops at normal incidence for a DCA network using Co atoms as metal coordination. Note that the preparation was imperfect since there is coexistance of network with small Co islands. Increasing the temperatureto 25 K practically closes the curve.*