Magnetism of cobalt nanoclusters on graphene on iridium

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(Dated: 17 February 2022)

The structure and magnetic properties of Co clusters, comprising from 26 to 2700 atoms, self-organized or not on the graphene/Ir(111) moiré, were studied in situ with the help of scanning tunneling microscopy and X-ray magnetic circular dichroism. Surprisingly the small clusters have almost no magnetic anisotropy. We find indication for a magnetic coupling between the clusters. Experiments have to be performed carefully so as to avoid cluster damage by the soft X-rays.

A noticeable effort is focused at theory level on understanding the magnetic properties of graphene in the presence of transition metals like Fe, Co or Ni. For example, the graphene-mediated exchange interaction between adatoms or impurities each holding a net magnetic moment has been explored and unconventional scaling with distance has been anticipated. Also, magnetic anisotropies as high as required for room-temperature magnetic storage have been predicted for Co dimers. So far, experimentalists investigated simpler systems, most prominently the interface between a ferromagnetic layer and graphene. These are indispensable for basic information on proximity-induced magnetic moments in carbon or the graphene/Co magnetic anisotropy. A step towards low-dimensional systems are assemblies of equally sized Fe, Co or Ni clusters comprising a 10-10 3 atoms, which are well adapted to the study of the size-dependent magnetic properties. Such clusters can be prepared on epitaxial graphene, e.g. on Ir(111), Rh(111), or Ru(0001) using graphene moirés as templates.

Using X-ray magnetic circular dichroism (XMCD), we explore the magnetism of Co clusters on graphene/Ir(111), which we relate to the cluster size and distribution by scanning tunneling microscopy (STM). Surprisingly, we find extremely weak magnetic anisotropies, although orbital moments are found to be slightly enhanced compared to bulk values. We also identify degradation of the clusters upon exposure to the X-ray beam.

Magnetic measurements and STM were performed in two interconnected ultra-high vacuum chambers; high resolution STM was performed using the same sample preparation in another system. Ir(111) was cleaned by cycles of Ar+ sputtering and flash annealing to 1500 K. Graphene on Ir(111) was prepared by chemical vapor deposition of ethene following a two step procedure yielding a closed and perfectly oriented monolayer. Co, Ir, and Pt evaporation was performed close to room temperature. The deposited amount θ [specified in ML, 1 ML being the surface atomic density of Ir(111)] was calibrated through STM for layers grown directly on Ir(111). XMCD was conducted at the ID08 beamline of the European Synchrotron Radiation Facility, monitored in the total electron yield (TEY) mode using (99±1%) circularly polarized light and up to ±5 T magnetic fields.

Through seeding with Pt and Ir, for small θ < 1 ML ordered arrays of Co clusters with the moiré pitch of 2.5 nm are formed, while for large θ > 1 ML still dense arrays are obtained, but each clus-
TABLE I. Orbital ($m_L$), spin ($m_S$) magnetic moments and their ratio ($m_L/m_S$) at 5 T with the X-ray beam perpendicular to the samples, which were prepared with different deposited amount of seeding and magnetic material ($\theta$), and the average cluster distance ($d$) for each sample (except for Pt$_{13}$Co$_{26}$, where $d$ is the moiré pitch).

| Sample     | $\theta$ (ML) | $d$ (nm) | $m_S$ ($\mu_B$) | $m_L$ ($\mu_B$) | $m_L/m_S$ |
|------------|---------------|----------|----------------|----------------|-----------|
| Pt$_{13}$Co$_{26}$ | 0.13/0.25      | 2.5      | 1.5 $\pm$ 0.2   | 0.22 $\pm$ 0.00 | 0.15$\pm$0.04 |
| Ir$_{50}$Co$_{500}$ | 0.17/1.70     | 4.8      | 1.7 $\pm$ 0.2   | 0.20 $\pm$ 0.02 | 0.12$\pm$0.03 |
| Co$_{2700}$   | 0.25          | 30       | 1.7 $\pm$ 0.2   | 0.18 $\pm$ 0.02 | 0.11$\pm$0.03 |

X-ray beam damage effects also small Co$_8$ clusters seeded by Ir$_4$ were probed (sample not listed in Table I).

The TEY was measured at 10 K and $\pm$5 T across the Co L$_{2,3}$ absorption edges for left- and right circularly polarized X-rays in perpendicular ($\perp$) incidence, at 5 T and 10 K. (b) XMCD signals for $\perp$ and 70° incidence (vertically shifted for clarity). Inset: XMCD signal normalized to absorption for Ir$_4$Co$_8$, at the beginning and after eight hours of irradiation.

$\theta$ (ML) $d$ (nm) $m_S$ ($\mu_B$) $m_L$ ($\mu_B$) $m_L/m_S$
Pt$_{13}$Co$_{26}$ 0.13/0.25 2.5 1.5 $\pm$ 0.2 0.22 $\pm$ 0.00 0.15$\pm$0.04
Ir$_{50}$Co$_{500}$ 0.17/1.70 4.8 1.7 $\pm$ 0.2 0.20 $\pm$ 0.02 0.12$\pm$0.03
Co$_{2700}$ 0.25 30 1.7 $\pm$ 0.2 0.18 $\pm$ 0.02 0.11$\pm$0.03

M-H loops display very weak anisotropies for all cluster sizes (Fig. 3). For Pt$_{13}$Co$_{26}$ clusters they do not seem to reach saturation and show no hysteresis down to 10 K (Fig. 3). A decrease of the zero-field susceptibility is observed as temperature increases (Fig. 3). Larger clusters have non-zero coercivity, which vanishes at 40$\pm$5 K.

The enhancement of $m_L/m_S$ for small clusters compared to the bulk is typical of small-size objects and arises from the local loss of symmetry (lower coordination or strain). The anisotropy of $m_L$ (data not shown for grazing incidence X-rays) is here neg-
ligible. Within the Bruno model linking the magnetic anisotropy energy (MAE) with the anisotropy of $m_L$ (arising from crystal structure, strain and interface hybridization), this is consistent with the nearly isotropic hysteresis loops. We do not consider dipolar anisotropy here, as the arrangement of the magnetic atoms in the seeded clusters is unknown. The observation of weak MAE whatever the environment (Pt or Ir seeding) and cluster size is surprising and contrasts with other low-dimensional magnetic systems on metal surfaces.

The absence of coercivity and the decrease of the zero-field susceptibility with increasing temperature is strong indications that the Pt$_{13}$Co$_{26}$ cluster lattices are superparamagnetic, as often the case for nanoclusters. Given the close-to-isotropic magnetic properties of the clusters, the M-H loops were fitted with a Langevin function, i.e., assuming no magnetic anisotropy. An additional slope was included in the fits, as discussed later. The result for the magnetic moment with increasing temperature, hinting at an origin different from superparamagnetism. An additional slope was included in the fits, as discussed later. The resulting magnetic moment $m = 107 \pm 19 \mu_B$ was found mainly independent of temperature, confirming the relevance of the fitting function. Dividing $m$ by the number of Co atoms per cluster gives $4.1 \mu_B$ per atom. This value is unphysical for metallic Co even assuming no magnetic anisotropy. The occasional coalescence of two or three clusters as visible in Fig. 1a cannot account for the high value of $m$ as only 15% of the islands are involved. The large $m$ value hence points to correlated spin blocks significantly larger than a single cluster, due to magnetic coupling between neighboring clusters. The origin of this coupling, dipolar, magnetic exchange either direct between Co atoms from neighboring clusters, or indirect through graphene, is at this stage speculative.

Let us also address the linear susceptibility (linear slope), dominating M-H loops above $\pm 2$ T (Fig. 3), which was taken into account in the fitting as an additional slope. The slope is independent from temperature, hinting at an origin different from superparamagnetism. Such linearity up to fields much higher than the expected spontaneous magnetization cannot be ascribed to dipolar energy. It may instead indicate exchange interactions favoring antiparallel or non-collinear magnetization arrangements. Whether this non-collinearity arises within each cluster in a hedge-hog fashion or from a block of neighboring clusters remains speculative with the present data.

For larger clusters (Ir$_{50}$Co$_{500}$ and Co$_{2700}$), the vanishing of coercivity (40±5 K) is presumably dominated by the blocking temperature of the largest clusters, around 10 nm in diameter and 3 nm in height for Co$_{2700}$ assemblies.

Finally, we discuss the degradation of the clusters upon exposure to X-rays. As documented by the inset of Fig. 2b, the XMCD signal decreases through 8 h irradiation by 40%, as derived from sum rules. Surfaces measured after the same waiting time, but not exposed to the beam, did not show any reduction of moment. Therefore surface contamination may be excluded. Consequently, the beam induces damage to the sample. Such a degradation is common for fragile magnetic species, but is usually not observed for metal clusters. We surmise that the X-ray beam promotes the decomposition of graphene by the clusters, similar to what happens at elevated temperature. Then, carbon enrichment of the clusters might be liable for the reduction of the Co XMCD signal.

We thank A. Fondacaro for technical assistance. T. M. and S. S. acknowledge financial support from the Deutsche Forschungsgemeinschaft (MI581/17-2), C.V.-V. from the Nanosciences Fondation. Research supported by the French ANR contract ANR-2010-BLAN-1019-NMGEM.

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