Supporting Information for: Complex Magnetic Exchange Coupling between Co Nanostructures and Ni(111) across Epitaxial Graphene

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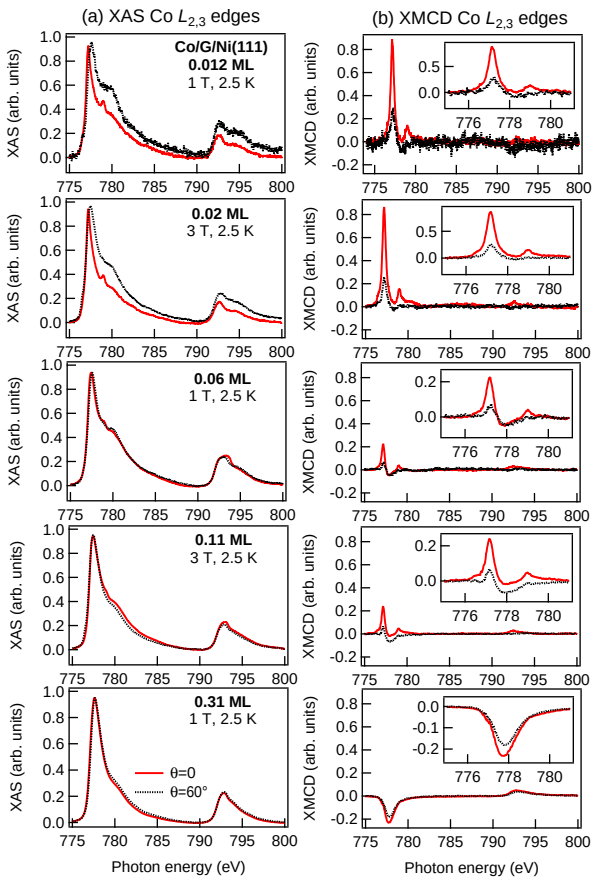

Figure S1: XAS and XMCD recorded at about 2.5 K and in a field $B = 1$ or 3 T, applied both at normal ($\theta = 0$, continuous red lines) and grazing ($\theta = 60°$, dotted black lines) incidence with respect to the sample surface: (a) XAS and (b) XMCD of Co/G/Ni(111) at the Co $L_{2,3}$ edges, for all measured Co coverages.

XAS and XMCD of Co/G/Ni(111) at intermediate Co coverages

Figure S1 shows the XAS [panel (a)] and XMCD [panel (b)] spectra at the Co $L_{2,3}$ edges as recorded, at $T = 2.5$ K and $B = 1 - 3$ T (i.e., above the magnetic saturation of Ni),

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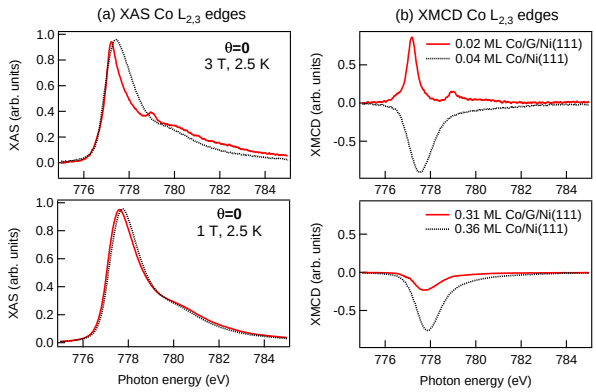

Figure S2: (a) XAS and (b) XMCD of Co/G/Ni(111) (continuous red line) and Co/Ni(111) (dotted black line), for selected Co coverages (top panel: low coverage, bottom panel: high coverage), recorded at $T = 2.5$ K and in a field $B = 1$ or 3 T, applied parallel ($\theta = 0$) to the Ni(111) direction.

on cobalt deposited at $T < 5$ K on G/Ni(111), for all measured Co coverages between 0.012 and 0.31 ML, and for a magnetic field applied parallel ($\theta = 0$) or almost perpendicular ($\theta = 60°$) to the Ni(111) direction. Associated with the increase of Co coverage, one observes a progressive disappearance of the multiplet structure and a loss of anisotropy of the XAS spectra [coverages above 0.02 ML in Fig. S1(a)], as expected when the Co-Co interaction becomes significant. The transition from positive to negative XMCD at the L_3 edge of Co occurs gradually [see Fig. S1(b)], and the negative spectral component at about 777.8 eV gains weight between the two positive spectral components at about 777.1 and 779 eV while crossing an intermediate regime (coverages around 0.06-0.11 ML), where individual atoms, small clusters, like dimers and trimers, and larger islands coexist.

Coverage dependence of the XAS and XMCD of Co/Ni(111)

The electronic and magnetic properties of Co/G/Ni(111) are quite different from those of Co atoms directly adsorbed onto the Ni(111) crystal, as exemplified in Fig. S2. Both for low and high coverages, the XAS of Co/Ni(111) at the Co $L_{2,3}$ edges [panel (a)] strongly resembles that of bulk metallic Co, and the sign of the XMCD at the L_3 edge [panel (b)]

Table S1: Total energy for a Co monolayer and a Co adatom on top-bridge G/Ni(111).[a]

	top 2		top 3		hollow	
	FM	AFM	FM	AFM	FM	AFM
Monolayer	+0.7	**0.0**	+0.3	+0.5	+40.2	+89.3
Adatom	+41.2	+34.8	+45.3	**0.0**	+245.8	+231.1

[a]As obtained for $U = 3$ eV and $J = 1$ eV.
The total energy is expressed in meV relative to the ground state.
FM (AFM) refers to parallel (antiparallel) alignment of the Co spin moment with respect to the Ni magnetization.

is always negative, as expected from the direct ferromagnetic coupling between Co and Ni in this case. It is striking to notice that, even at the highest coverage of 0.31 ML, where direct Co-Co magnetic interactions are significant, Co/G/Ni(111) shows a strongly reduced XMCD as compared to Co/Ni(111), even at fields corresponding to the magnetic saturation of the Ni crystal.

Co adatoms and monolayer on top-bridge stacked graphene on Ni(111)

We have performed DFT calculations of a single Co adatom and a Co monolayer (ML) adsorbed on a top-bridged stacked graphene layer on Ni(111). This type of stacking is the second most abundant after the top-fcc.[?] In the case of top-bridge stacking the two C atoms in the graphene layer have the same nearest neighbor coordination, as far as the most superficial Ni layer is concerned, while they differ only in the relative position with respect to the second and third Ni layers from the surface. More precisely, C atoms sit at sites that have in-plane coordinates in a bridge position with either the second or the third Ni layer from the surface. Co adatoms on top of such C atoms are therefore labeled with 'top 2' or 'top 3', respectively. Similarly to the top-fcc stacking, we have characterized both ferro- (FM) and antiferromagnetic (AFM) couplings between Co and Ni spins at the three lowest

energy high-symmetry adsorption sites.

We observe that for a Co ML, the two top adsorption sites have very similar adsorption energies, and FM and AFM solutions are nearly degenerate (see Table S1). For the hollow adsorption site, a clear preference towards FM coupling with the Ni magnetization is observed. On the other hand, when moving to the adatom limit, a clear preference towards AFM coupling is observed for all the adsorption sites. Therefore the analysis of the top-bridge stacking shows that the sign of the coupling is generally FM for the monolayer and AFM for the adatom case. This is the same trend that we find for the top-fcc stacking, as discussed in the main text. Moreover, the spin moments attained by Co both in the monolayer and adatom limits are very similar to the ones found for the top-fcc graphene stacking.