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# Magneto-optical reflection spectroscopy on graphene/Co in the soft x-ray range

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**Abstract.** The existence of ferromagnetic ordering in graphene on cobalt is demonstrated by means of resonant magnetic reflection spectroscopy exploiting the transversal magneto-optical Kerr-effect (T-MOKE). Using linearly polarized synchrotron radiation in the soft x-ray range with energies spanning the carbon 1s edge, the  $\pi$ - and  $\sigma$ - bonds of graphene were excited individually, showing that magnetism in graphene is carried by the  $\pi$  – orbitals. Magnetic signals were detected over a wide energy range from 257 – 340 eV with a T-MOKE peak value of 1.1 % at the  $\pi$  – resonance energy near 285 eV. By comparison with corresponding spectra measured at the 2p edges of the Co substrate, a large induced magnetic moment of 0.14  $\mu_B$  was derived for graphene. Individual hysteresis curves monitored at the Co 2p and C 1s edges show that the carbon magnetism is induced by the Co substrate.

## 1. Introduction

Graphene is a promising candidate material for novel electronic devices [1]. Its properties result from the layered structure of carbon atoms which gives rise to a large anisotropy in its structural and electronic properties due to the anisotropic bonding characteristics [1]. The carbon atoms in the basal plane are bound together by strong covalent  $\sigma$ -bonds while the  $\pi$ -bonds are oriented perpendicular to the substrate. This anisotropy can be probed best by polarization- and reflection spectroscopy using linearly polarized light. Setting the electric field vector parallel to the respective orbitals allows to probe individually the  $\pi$ -states and  $\sigma$ -states, respectively [2]. Recently magnetism was detected in carbon based materials, graphite and graphene which could offer access to new technological applications, e.g. in the field of spintronics or data storage [3, 4]. However, the origin of this magnetism has still to be identified. In graphite (HOPG) it is believed to result from the defect structures, *i.e.* from localized electron states at grain boundaries which form arrays of point defects [4]. In single layer graphene grown on SiC ferromagnetic behavior at room temperature could be detected after hydrogenization [5]. For technical applications having graphene grown on magnetic,

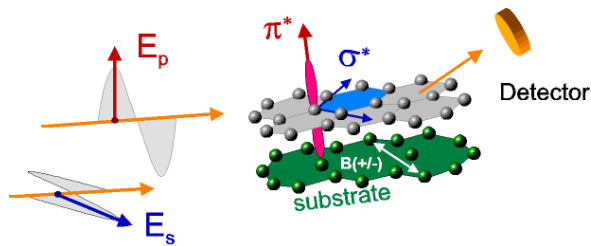


metallic substrates seems to be a fruitful approach [6, 7]. However, a clear understanding of the interaction of carbon atoms with the metallic substrate is still missing.

Up to now, the applied magnetic detection techniques were not able to 1) unambiguously identify the localization of magnetic moments at the carbon atoms and 2) to identify the influence of  $\pi$ - or  $\sigma$ -bonds. A promising method for solving point 1), i.e. separating the magnetic response of possible metallic impurities from that of carbon, is the element-selective excitation of carbon at the C 1s state with polarized synchrotron radiation (SR) [8]. Up to now only x-ray magnetic circular dichroism (XMCD) measurements of graphene on Ni exist which suggest a magnetic moment of carbon in the order of  $0.05 - 0.1 \mu_B$  [7]. However, these XMCD experiments suffer from the fact that the polarization state of circularly polarized SR varies dramatically when tuning the photon energy across the C 1s edge caused by the unavoidable carbon contamination of the optical elements in the beamline [9]. To solve point 2) a spectroscopy is necessary which allows to probe the orientation of bonds. Both tasks can be tackled by our magneto-optical polarization- and reflection spectroscopy.

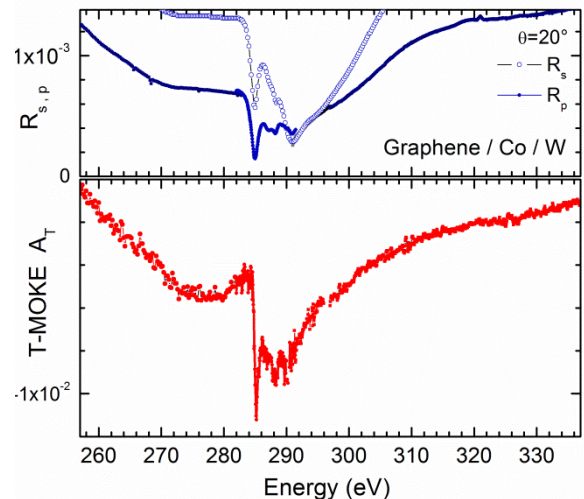
## 2. Experiment

The experimental setup for our magneto-optical reflection spectroscopy is shown in figure 1. The incident intensity  $I_0$  is reflected partially at the graphene surface and partially, after transmission of the graphene layer, at the metallic substrate. Upon reflection a phase shift appears at the graphene surface as well as at the metallic substrate with difference  $\alpha$  between these phase shifts. An additional phase shift due to the optical path length is negligible for the extremely thin graphene layer. The total reflected intensity  $I$  is described by  $I/I_0 = R_G + (1 - R_G)T_G^2 R_M + 2|r_G r_M|(1 - R_G)^{0.5} T_G \cos \alpha$  with reflectance  $|r_G|^2 = R_G$  and transmittance  $T_G$  of graphene and  $|r_M|^2 = R_M$  the reflectance of the substrate acting as a mirror and  $\alpha$  the phase shift of light reflected at the graphene surface and the substrate, respectively. The transmission through the graphene dominates over the reflectance at the graphene top surface since  $R_G \approx R_M/10$ . This result, obtained from independent reflection experiments of graphene, has been confirmed by model calculations using the computer code REFLEC [10] and optical constants of carbon and cobalt from Henke data table [11].



**Figure 1.** Experimental setup for detecting reflection and T-MOKE, applying transversal magnet fields  $B(+/-)$  to graphene on the Co substrate.

**Figure 2.** Top: Reflectance for  $p$  and  $s$ -geometry, bottom: T-MOKE spectrum deduced from  $R_p$  ( $B+/-$ ).

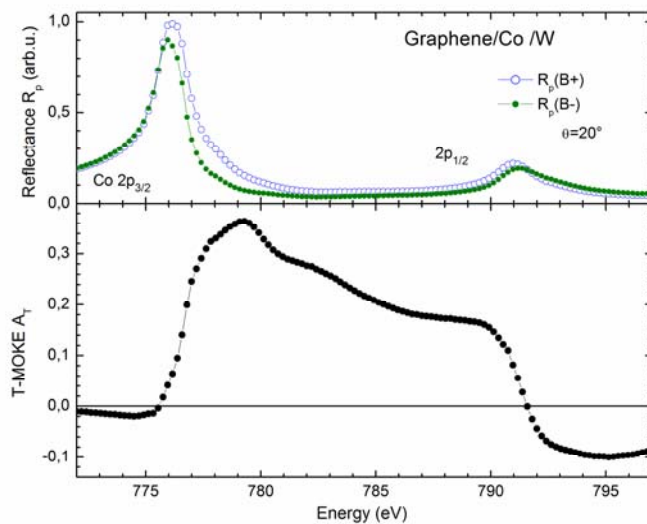


The experiments were performed at the undulator beamline UE56-2-PGM2 at BESSY [12] using the BESSY ultrahigh-vacuum polarimeter chamber [13]. The spectral resolution near 290 eV was set to  $E/\Delta E=2000$  and the accuracy of the absolute energy calibration was better than 0.1 eV. The electric field vector  $E$  of the linearly polarized incoming light could be set alternatively parallel to the  $\pi^*$ -orbitals ( $E_p$  in figure 1,  $p$ -geometry) or perpendicular to the  $\pi^*$ -orbitals ( $E_s$ ,  $s$ -geometry) with fixed

angle of incidence  $\theta = 20^\circ$ , measured to the surface. The samples were monolayer graphene deposited on 6.0 nm Co (0001) grown on W(110) substrate characterized prior to measurement by STM and LEED [6]. All recorded spectra were corrected for contributions from high order light applying a procedure described in Ref. 14. Any in-plane magnetization geometry could be set by *in situ* rotation of permanent magnets with maximum field strength of 250 mT [15]. Hysteresis curves were achieved by applying a solenoid creating in-plane fields of up to +/-50 mT.

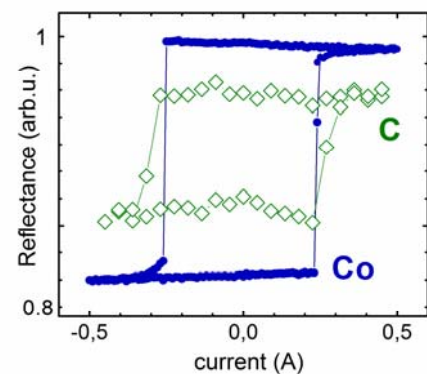
### 3. Results

The absolute reflectance  $R_p$  is plotted in figure 2, top, for p-polarization geometry ( $E_p$  in figure 1). At the  $\pi^*$ -resonance (285.0 eV) the measured reflectance decreases due to the decrease of transmission of the graphene layer and accompanied decrease of light reflected from the metallic Co substrate. A second minimum in the reflectance appears at the  $\sigma^*$ -resonance (291.2 eV). Since the electric field  $E_p$  is oriented parallel to the  $\pi^*$ -orbitals excitations from C  $1s$  to  $\pi^*$ -states dominate. For electric field vector  $E_s$  oriented parallel to the  $\sigma^*$ -orbitals (s-geometry, figure 1) the minimum at 291.2 eV is more pronounced ( $R_s$  in figure 2, top). The magnetization of graphene was probed by T-MOKE [8] scanning across the C  $1s$  edge. The normalized difference signal  $A_T = (R_p(B+) - R_p(B-)) / (R_p(B+) + R_p(B-))$  of the reflectance  $R_p(B(\pm))$  is monitored for two anti-parallel in-plane magnetization directions  $B(\pm)$  perpendicular to the light's scattering plane (figure 1). The obtained T-MOKE spectrum  $A_T$  (figure 2, bottom) clearly shows magnetic signals over a wide range across the C  $1s$  edge. Strongest effects of 1.1% occur at the  $\pi^*$ -resonance while at the  $\sigma^*$ -resonance only small effects are detected. This clearly shows that the magnetism in graphene is carried by the  $\pi$ -orbitals. The appearance of magnetic signals even far below the  $\pi^*$ -resonance is explained by the typical enhancement of magnetic signals in reflection spectroscopy at low reflectance values due to normalization [16]. Exactly this is the case for carbon showing small  $R_G$  below the  $\pi^*$ -resonance [17].



**Figure 3.** Top: Reflected Intensity across the Co  $2p$  edge of graphene on Co/W of p-polarized light for two transversal magnetizations  $B(\pm)$  at incidence angle  $\theta = 20^\circ$ . Bottom: Deduced T-MOKE  $A_T$ .

For comparison of magnetism in graphene and the underlying Co substrate T-MOKE spectra were recorded across the Co  $2p$  edges (figure 3). The reflectance  $R_p$  is resonantly enhanced at the Co  $2p_{3/2}$  and  $2p_{1/2}$  edges. Strong differences at and in between these edges appear for inverted transversal magnetic fields (figure 3, top). These lead to large T-MOKE values of up to 37% in between the edges (figure 3, bottom). Note that the magnetic T-MOKE value  $A_T$  is increased in between the edges due to normalization on small reflectance values as typical for Co films [18]. However, resonant excitation of



**Figure 4.** Hysteresis curves of graphene and Co recorded with  $R_p$  as function of the coil current at the C  $1s$  and at the Co  $2p_{3/2}$  edge.

Co atoms occurs at the Co  $2p_{3/2}$  edge (776.35 eV). At this energy the relevant T-MOKE signal  $A_T = 0.1$  has to be taken for comparing magnetic moments as discussed below.

Exploiting the T-MOKE, two element specific hysteresis loops were recorded by setting the photon energy first to the Co  $2p_{3/2}$  resonance at 775.75 eV and then to the C  $1s$  resonance energy (286.3 eV) and detecting the reflected intensity as function of the applied magnetic field strength (figure 4). These hysteresis loops show the individual magnetic behaviour of carbon atoms in graphene demonstrating that Co induces the ferromagnetism in graphene which is harder than in Co.

The magnetic moment of carbon atoms in graphene was deduced by comparing the strength of T-MOKE data at the C  $1s$  edge of graphene ( $A_T(C) = 0.011$ ) with T-MOKE data exactly at the Co  $2p_{3/2}$  edge  $A_T(Co) = 0.1$ . From the ratio of the asymmetry parameter  $A_T(C)/A_T(Co)$  and the magnetic moment of Co  $\mu_{Co} = 1.76\mu_B$  we obtain the magnetic moment of carbon  $\mu_C = 0.14 \pm 0.03\mu_B$ . In this calculation a correction factor of 0.87 enters which takes into account the small difference in the polarization power between carbon at the C  $1s$  edge and cobalt at the  $2p$  edge. This polarization power enters the T-MOKE signal and must be considered according to the procedure described in Ref. 16. The obtained magnetic moment of graphene is a factor of three larger than the value obtained for amorphous C-layer in a Fe/C multilayer [19]. This is surprising in view of the larger magnetic moment of Fe compared to that of Co. We explain this larger magnetic moment due to the collectively aligned  $\pi^*$ -orbitals in graphene, confirmed by polarization analysis [17], in contrast to the situation in the polycrystalline C-layers of Fe/C [19].

In summary we observed ferromagnetic order in graphene on Co by T-MOKE spectroscopy across the C  $1s$  edge and determined experimentally an induced magnetic moment of  $0.14\mu_B$  on carbon which is based on the hybridization of Co  $3d$  with carbon  $\pi^*$ -orbitals.

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