

Direct observation of local ferromagnetism on carbon in C/Fe multilayers

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Abstract. – An element-selective investigation of magnetism on carbon in the vicinity of Fe atoms in a C/Fe multilayer is reported. We utilize resonant magnetic reflectivity of circularly polarized synchrotron radiation which allows us to distinguish unambiguously the local magnetism on carbon from that on Fe through individual core-level excitations. Clear magnetic signals of carbon are obtained by exploiting the standing-wave technique. Hysteresis loops of individually excited C and Fe atoms demonstrate ferromagnetism of C at room temperature with a moment of $\approx 0.05\mu_B$ induced by adjacent Fe atoms.

The possibility of ferromagnetism at room temperature in carbon-based materials as, *e.g.*, doped graphite, synthetic fullerene C₆₀, and carbon composites, such as a graphite-containing meteorite, has recently been concluded from bulk magnetic measurements [1–4]. Ferromagnetism of carbon would indeed have far-reaching consequences in our understanding of this material indispensable to life science as well as for technology, *e.g.*, as applications of magnetic carbon in spin electronics. Additional support for the occurrence of magnetic carbon has been provided by theoretical studies that predicted a magnetic instability for carbon [5] and magnetism at graphite surfaces and 2-dimensional sheets [6–8]. Yet, in spite of the research efforts undertaken lately, it could not be proven whether the magnetism detected in bulk magnetization measurements is intrinsic to carbon rather than being due to minute amounts of magnetic impurities. This is a drawback of the so far used experimental techniques which average over the complete sample, *i.e.* the carbon including impurities. Thus a technique is necessary which separates the signal of C by suppressing the signal of impurities. The detected magnetic signals of C are typically very weak and could therefore not rule out a parasitic signal of magnetic impurities, and thus did not permit an unambiguous detection of magnetism on the carbon atoms. For the description of the origin of magnetism on carbon in terms of the electronic configuration, one has to consider the predicted spin polarization of p_z

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orbitals at graphene surfaces [6] as well as magnetism, induced by adjacent magnetic atoms, something which is well known, *e.g.*, from CoPt [9].

To investigate the occurrence of ferromagnetism on carbon and its electronic origin we selected a C/Fe multilayer system. In order to probe locally the magnetization of carbon, we utilized the element selectivity of X-ray magneto-optical reflectivity of polarized synchrotron radiation (see, *e.g.*, refs. [10–14]). Element selectivity is achieved by tuning the energy of the photon beam used for excitation to the individual core-level absorption edges of the atomic constituents, *e.g.*, of carbon (C $1s$ edge near 284 eV) or iron (Fe $2p$ edge near 705 eV), leading to a local, resonant excitation exhibiting clearly separated signals from the individual elements C and Fe, respectively. Thereby we can unambiguously distinguish whether the local magnetism resides on C or not.

For the detection of magnetism we exploited the X-ray magnetic circular dichroism (XMCD) observable from magnetized samples in reflection [10, 14] of circularly polarized synchrotron radiation. The XMCD asymmetry parameter A is a measure of the local ferromagnetic order. It is defined as $A = (R^+ - R^-)/(R^+ + R^-)$, *i.e.*, the normalized difference of the reflected intensities (R^+, R^-) for two orientations (parallel, anti-parallel) of the sample magnetization M and the photon helicity [14]. The XMCD asymmetry scales linearly with the local magnetization of the probed atoms [10].

While former experiments suffered from extremely weak signals, the choice of the C/Fe multilayer system is especially advantageous, because the periodicity of the multilayer enables the creation of standing X-ray waves [15, 16]. These standing X-ray waves cause a collective excitation of the individual layers at the corresponding Bragg angles and, as a result, we can easily achieve large and clear signals from carbon. Furthermore, by scanning the angle of incidence across the Bragg angle, the center of excitation is tuned from the carbon to the Fe layers through the interface providing insight in the magnetism at the interface.

The investigated sample was a magnetron sputtered multilayer of 100 double layers of Fe ($d_1 = 2.55$ nm) and C ($d_2 = 0.55$ nm), capped with 2.5 nm Al. The outermost Fe layer was oxidized to an extent of $25\% \pm 5\%$, while all other Fe layers were non-oxidized. This depth profile was obtained by X-ray photoemission spectroscopy (XPS) using Al-K- α radiation, after sputtering the sample surface [14]. The multilayer structure offers a second advantage in addition to the creation of standing waves. The extremely thin carbon layers lead to a large ratio of C-Fe interfaces to C volume. This ratio is increased further by the naturally appearing mixture of C and Fe at the interfaces, expressed by the average roughness. For our multilayer it was determined to be 0.35 nm from a fit to X-ray reflectivity of Cu K- α radiation [14]. The in-plane saturation magnetization of our sample was $M = (3.01 \pm 0.03) \times 10^{-3}$ emu, determined by SQUID measurements.

The room-temperature resonant magnetic reflection experiment was performed at BESSY, Berlin, using the elliptical undulator beamline UE56/1-PGM. The degree of circular polarization of the X-rays was 100% at the C $1s$ edge and 90% at the Fe $2p$ edge [17]. By employing the BESSY polarimeter chamber [18], quasi-simultaneous detection of incident and reflected light was performed in order to gauge the absolute reflectance. The angle of incidence θ could be tuned from 0° (grazing incidence) to 85° (near-normal incidence) while a GaAsP photodiode moved by 2θ to monitor the reflected beam. A magnetic coil system supplied variable magnetic fields between ± 500 Oe parallel to the sample plane and the scattering plane.

The reflectance spectra of circularly polarized light across the C $1s$ edge of the magnetically saturated sample are shown in the top panel of fig. 1 for two angles of incidence. Both spectra display 4 distinct peaks between 282.5 eV and 290.5 eV, which are assigned to resonant excitations, related to transitions from C $1s$ to π^* -states [19]. Excitations to σ^* -states, which should appear between 290 eV and 300 eV, are much less pronounced. From the predominance

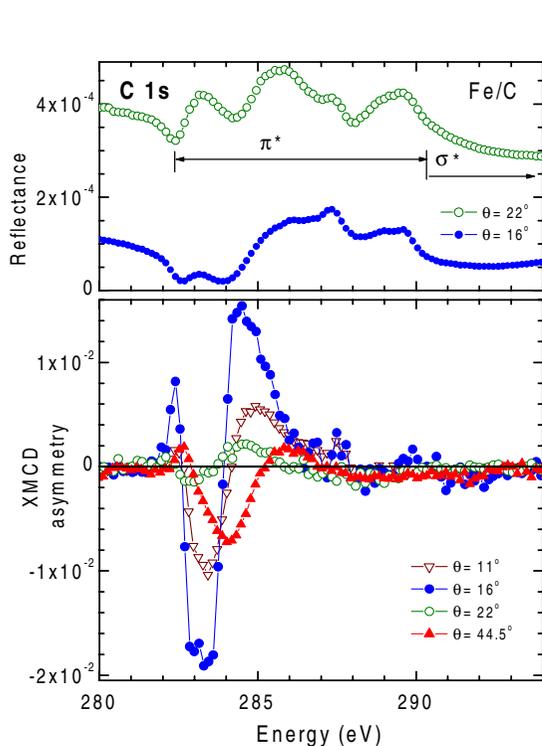


Fig. 1

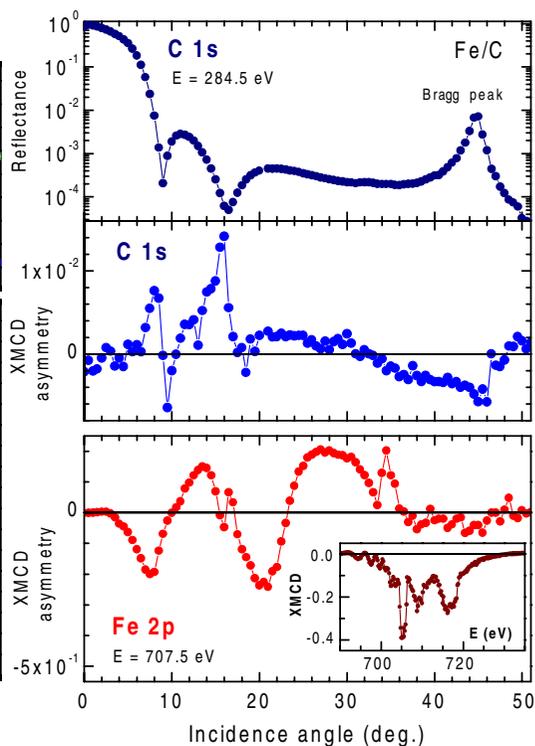


Fig. 2

Fig. 1 – Top: reflectance spectra of circularly polarized synchrotron radiation from a C/Fe multilayer for two different angles of incidence across the C 1s absorption edge. Bottom: the local ferromagnetism of C is detected by the magnetic asymmetry (XMCD) signal A . Note that the XMCD signal appears only within the energy region where resonant excitations from the C 1s core level to the π^* valence states occur.

Fig. 2 – Top: reflectance of the C/Fe multilayer as a function of the angle of incidence for fixed photon energy at the C 1s edge. The reflectance minima at 9° and 16° are due to near-surface destructive interference. At the Bragg peak (44.5°) a collective excitation of the C layers is achieved by creating X-ray standing waves. Middle: the magnetic XMCD asymmetry signal measured at the C 1s edge *vs.* angle of incidence. The XMCD signal proves that local ferromagnetism on C is observable for a wide range of incidence angles. Large XMCD values are obtained for the collective excitation of C atoms at the Bragg peak (44.5°) as well as at inclined incidence (9° , 16°). Bottom: the local ferromagnetic XMCD signal of Fe measured at the Fe 2p edge as a function of the incidence angle. The inset shows the XMCD spectrum across the Fe 2p edge at $\theta = 7^\circ$. The angular dependence of the XMCD asymmetry exhibits large values in between and close to the first Bragg peak ($\theta = 16^\circ$) and second Bragg peak ($\theta = 34^\circ$), where the Fe atoms are collectively excited.

of transitions to π^* -states over those to σ^* -states, we deduce that the sp^2 -coordination of carbon predominates over the sp^3 -coordination [19]. This, in turn, indicates that in the C/Fe multilayer layered bonding (graphite-like) of carbon is favoured over tetrahedrally coordinated bonding (diamond-like). Upon reversal of the magnetization the reflectance changes, as shown by the XMCD asymmetry A (fig. 1, bottom). Peak values of up to 2% near the first two reflection structures between 282.5 eV and 285.5 eV are easily detectable. Away from the

C 1s absorption edge, the asymmetry fades out and no magnetic signal is observed. These observations are decisive since they prove for the first time directly the magnetic response of carbon, which is unmistakably separated from the magnetic signal of Fe. As shown below, the Fe signal appears at energetically well-separated excitation energies between 690 eV and 730 eV. In addition, the XMCD spectrum reveals that the major magnetic response stems from transitions to the π^* -states, while transitions to the σ^* -states yield practically no magnetic signal. The occurrence of spin-polarization on carbon appears thus to be connected to the graphite-like sp^2 -coordination.

By varying the angle of incidence of the X-rays, the sampling depth is tuned from near surface to volume excitation. The angular dependence of the reflectance is shown in fig. 2 (top) for a fixed resonance energy at the C 1s edge. We observe the usual decrease of the reflectance with increasing angle of incidence. The strong reduction of the reflectance at $\theta = 9^\circ$ and $\theta = 16^\circ$ is due to destructive interference occurring within the three uppermost layers which are Al, C and oxidized Fe. As expected, at the Bragg angle ($\theta = 44.5^\circ$) of the multilayer system a strong increase of the reflectance is observed due to the creation of soft-X-ray standing waves. The angular dependence of the corresponding magnetic asymmetry is shown in the middle panel. It is negligible at grazing incidence ($\theta < 5^\circ$), where the penetration depth of the X-rays perpendicular to the sample surface is very small and where the reflectance is dominated by the non-magnetic aluminium cap layer [14]. In this region no magnetic information from C is obtained. The penetration depth of the light and thus the number of reflecting layers increases with the angle of incidence. Although the difference in the absolute reflectance spectra R^+ and R^- is small at 9° and 16° , respectively, larger signals are observed in the XMCD asymmetry (fig. 2, middle part). This increase stems from the normalization on an average reflectance which is rather small due to interference, leading to a reduction of the non-magnetic contribution to the signal. While the excitation of surface near layers leads to sharp peaks in the magnetic asymmetry due to destructive interference effects, broader structures are obtained at larger angles of incidence (fig. 2, middle part). Here predominantly carbon of the sample volume is probed, most pronounced at the Bragg angle where the carbon layers are collectively excited leading to a relatively large magnetic asymmetry of up to 0.6% (see figs. 1 and 2).

The individual magnetization behavior of Fe is obtained from reflectance spectra measured at the Fe 2p edge. The inset of fig. 2 (bottom) shows the XMCD spectrum measured at 7° , thus probing the uppermost 4–5 nm of the sample. As expected, the partially oxidized Fe in the uppermost Fe layer causes a subsidiary splitting of the $2p_{3/2}$ and $2p_{1/2}$ resonances due to multiplet contributions [20]. The angular dependence of the XMCD measured at the Fe 2p resonance energy is shown in the bottom part of fig. 2. The magnetic asymmetry reaches huge values of up to $A = 0.24$. These occur in particular in between and close to the first Bragg peak ($\theta = 16^\circ$) and second Bragg peak ($\theta = 34^\circ$), where the Fe atoms are collectively excited [14].

Hysteresis loops provide the classical proof of magnetism. The hysteresis loop pertaining to the collective excitation of carbon, measured at the 1s resonance energy is shown in fig. 3. It was obtained by monitoring the reflected intensity as a function of the applied magnetic field, given by the current of the coils. A ferromagnetic magnetization loop with a coercivity of (1.7 ± 0.2) mT is observed. The carbon hysteresis loop follows evidently that of the Fe atoms, recorded at the Fe 2p edge at 705.6 eV. These hysteresis loops demonstrate directly the local influence of Fe atoms on the magnetism of C atoms. Note that the signals are obtained from the individual elements, at distinctly different core level excitation energies. To investigate the influence of oxidized Fe on the magnetism of C, we set the energy to the C 1s edge and the angle of incidence to 9° and to 16° , probing particularly the interface between C and the oxidized first Fe layer. The corresponding hysteresis loops do not show a remarkable difference compared to that recorded for C in the samples volume. From this we conclude

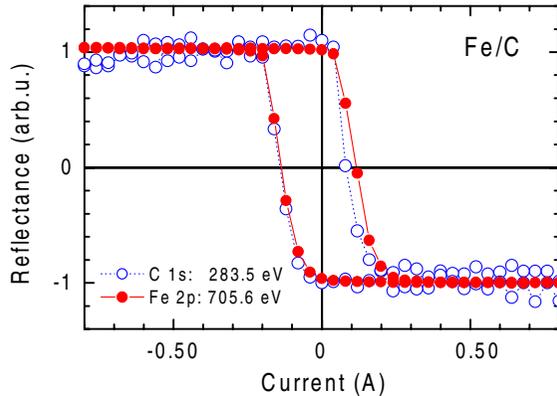


Fig. 3 – Element-specific hysteresis loops of carbon and of Fe, recorded at their respective core-level edges and Bragg angles (44.5° for C and 16° for Fe). The hysteresis loop of C proves ferromagnetism on carbon, whose magnetization follows that of Fe.

that the influence of ferro-magnetic Fe dominates over that of FeO. As a result, C shows local ferromagnetic behaviour even in the vicinity of oxidized Fe.

Previous theoretical studies addressed the origin of magnetism on C [5–8], yet its full elucidation is still awaiting. It was suggested that magnetism is an intrinsic feature of graphite [1,6]. An indication for ferromagnetism intrinsic to carbon has been deduced from the Curie temperature of 580 K that was associated with C, since it could not be attributed to known ferromagnetic inclusions [3]. From our study, we conclude that ferromagnetism can easily be induced on C through the interaction with a ferromagnetic material. This observation is in agreement with a possible instability towards magnetism [7,8]. Furthermore, our study shows clearly that a magnetic signal is obtained only from the π^* -states above the Fermi energy and not from the σ^* -states (see fig. 1, bottom). Magnetism thus appears to be related to the hybridization of the Fe 3d orbitals and the C- p_z orbitals which are normal to the graphene-type layered sp^2 -coordination. The induced spin polarization of these C- p_z orbitals appears to be the key to magnetism in C-based materials. While spin polarization induced through adjacent Fe atoms is thus essential, the recorded magnetic signal is undoubtedly that of C and not a residue of the Fe magnetic signal. The reflectance at the C 1s edge exhibits the typical π^* - and σ^* -related structures that are observed in numerous C-containing substances [19]. Carbon has a broad, open sp -hybridized shell, for which *ab initio* calculations showed that the π^* - and σ^* -bands extend far above the Fermi energy (see, *e.g.*, [21]), which obviously cannot be filled by Fe-donated electrons. To estimate roughly the local magnetic moment of C in our C/Fe multilayer, we employ the ratio of the Fe and C asymmetry parameters A_{Fe} and A_{C} , respectively. These are chosen from the respective first Bragg angle measured at the C 1s absorption edge at 44.5° and at the Fe 2p edge at 16° , respectively. At these Bragg angles, a collective excitation of the individual elements is achieved and the absolute reflectances are comparable. Taking $A_{\text{C}} = 0.0033$ and $A_{\text{Fe}} = 0.175$ just before the Bragg peak, we obtain $A_{\text{Fe}}/A_{\text{C}} = 53$. At the Bragg peaks we find $A_{\text{Fe}}/A_{\text{C}} = 0.18/0.0056 = 32$. Using the magnetic moment of bulk Fe ($\mu_{\text{Fe}} = 2.21\mu_{\text{B}}$), a local magnetic moment $\mu_{\text{C}} = 0.042\text{--}0.067\mu_{\text{B}}$ on carbon is estimated. These values are larger than that ($\mu_{\text{C}} = 0.02\mu_{\text{B}}$) estimated by Murata *et al.* [22], and comparable to that ($\mu_{\text{C}} = 0.05\mu_{\text{B}}$) deduced from the meteorite sample by Coey *et al.* [4].

In conclusion, the present investigation demonstrates that carbon atoms can be ferromagnetic in the presence of Fe atoms. This was observed directly by exploiting the element selectivity of X-ray magnetic spectroscopy to a C/Fe multilayer. Hysteresis loops recorded at the respective core-level excitations of C and Fe unambiguously prove ferromagnetism on C that follows that of Fe. We believe that the sp^2 -coordination of carbon is important for the magnetism in C. For further unravelling the intricacies of pure carbon magnetism, we consider as next step the investigation of C/X multilayers with the non-magnetic element X. Exploiting the reported technique on such multilayers, strong signals from C would be expected to allow insight in the relevance of C π - and σ -bonding at the interfaces for the magnetism.

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