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# Low-energy μSR and SQUID evidence of magnetism in highly oriented pyrolytic graphite

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ABSTRACT

Low-energy muon spin rotation and SQUID magnetization measurements were performed on proton-irradiated and non-irradiated highly oriented pyrolytic graphite samples. The samples were found to be ferromagnetic above and below room temperature and to include a substantial temperature-dependent surface contribution. Assuming uniformity, the thickness of the magnetic surface layer was estimated to be 13(2) nm. The discovered surface magnetism is intrinsic and not due to irradiation.



## 1. Introduction

The possibility that metal-free organic compounds can show ferromagnetic behavior at room temperature is both unexpected and intriguing. Therefore, it has attracted an increased scientific interest, related not only to the theoretical fundamentals of magnetism, but also to possible novel technological applications. In particular, the possible existence of room temperature magnetic order in a simple system like carbon is significant since it allows a more direct comparison between theoretical predictions and experiments. Ferromagnetic-like loops in the magnetization of virgin highly oriented pyrolytic graphite (HOPG) samples show saturation values in the range $1-25\times10^{-4}$ emu/g [1], whose origin remains unclear. SQUID and X-ray circular magnetic dichroism measurements performed on proton bombarded oriented graphite [2] and on thin carbon films [3] support the hypothesis that this magnetism could be induced by defects. Several theoretical studies based on the influence of defects and of hydrogen [4] were recently developed to explain the experimental results.

The origin of the magnetic order observed in virgin graphite is still elusive. Simple estimates indicate that several parts-per-million of iron and/or magnetite could account for such measured values. Despite indirect indications that speak against impurities [1], a certain amount of skepticism still exists. To shed more light on the nature of the HOPG magnetism, we use the novel low-energy muon spin rotation (LE-μSR) technique [5]. μSR is a high-sensitivity magnetic local probe technique which can detect magnetic moments as small as $10^{-3}$–$10^{-4}\mu_B$. In a μSR experiment, an ensemble of nearly 100% spin-polarized muons is implanted in the sample. The muons stop and precess around the local magnetic field. The temporal evolution of the spin polarization (or asymmetry) of the muon ensemble (μSR signal) is monitored by detection of anisotropically emitted decay positrons. From this, valuable information regarding the intensity, directionality and dynamics of the internal magnetic fields can be deduced. LE-μSR advantages include: (a) insensitivity to small contaminations of any kind, since the contribution from each magnetic phase is weighted by its magnetic volume fraction, (b) microscopic depth selectivity, and (c) ability to measure at zero applied field (ZF). Our LE-μSR and SQUID measurements on HOPG are reported in the present work.

## 2. Experimental details

Two HOPG samples of 0.4° rocking-curve width were supplied from Advanced Ceramics company. Each of them was made of four pieces ($10\times10\times0.3\,mm^3$ each) glued on a Ag-sputtered LE-μSR sample plate. One sample was irradiated with 2 MeV proton beam (180 nA ion current) at room temperature ($12\times12$ spots of ~1.5 mm diameter each, covering ~64% of the whole sample surface). The nominal fluence was ~0.1 nC/μm², i.e. ~180 μC per spot. The magnetic impurity concentration measured during the irradiation process was constantly $\lesssim$1 ppm. Both HOPG samples were measured by LE-μSR at 20 K, whereas the irradiated sample

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was also measured at 300 K. At the lowest measured muon energy, 0.5 keV, transverse field (TF) data at $H = 100$ Oe were collected as well. Two positron detectors (left-right), arranged parallel to the edge of sample, were used in the experiment. As a result, we were insensitive to components of the magnetic fields which do not lie along that particular axis. Deceleration of the moderated incoming muons down to the desired implantation energies (0.5–10 keV) was achieved by connecting the sample plate to a high voltage power supply. After the LE-μSR measurements, SQUID magnetization measurements were done on different ~14 mg, $\sim 5 \times 5 \times 0.3\,\mathrm{mm}^3$ fragments, cut out from the original sample pieces.

## 3. Experimental results

The muon implantation profiles in HOPG were calculated using the Monte-Carlo TRIM.SP package (Fig. 1), proven to be reliable in previous LE-μSR works [6]. For the irradiated sample, the LE-μSR signals for several muon implantation energies, at 20 and 300 K, are depicted in Fig. 2. The signals for 5 and 10 keV (not depicted) muon energies show no relaxation within statistics, implying that no magnetic fields are sensed by muons stopping at ~30–80 nm below the HOPG surface (Fig. 1). Conversely, for muons impinging with lower kinetic energies (0.5, 1.5, and 2.5 keV), a considerable relaxation is observed. This could be partially attributed to magnetic fields sensed by muons stopping below the HOPG surface. However, at low energies (<5 keV), the LE-μSR signal is affected by two undesired contributions arising from muons decaying without reaching the sample, and muons which enter the sample and backscatter before stopping. These instrumental contributions to the signal increase with decreasing muon implantation energy and have a non-trivial influence on the relaxation of the asymmetry as a function of energy. Nevertheless, none of these artifacts depends on sample temperature, and therefore cannot account for the observed temperature-dependent signal behavior. This fact is clearly confirmed by 1 keV data on a non-magnetic Au sample, where practically the same signal is observed at two very different temperatures, 20 and 250 K (see Fig. 3).

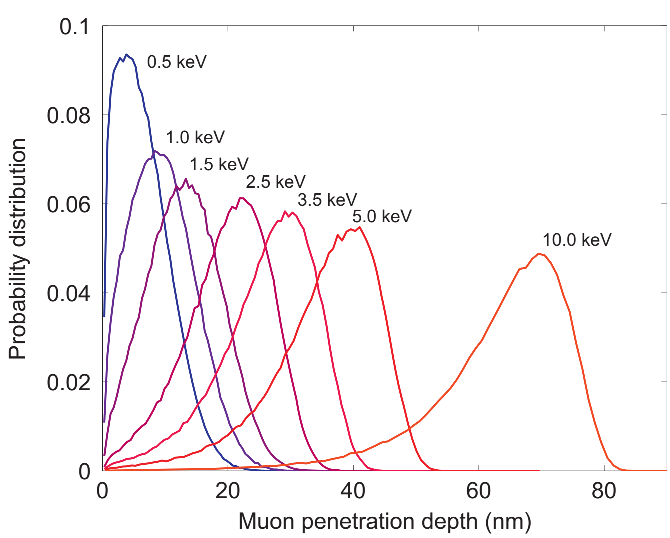


**Fig. 1.** The muon implantation profiles in graphite calculated for different incident muon energies assuming a mass density $\rho = 2.27\,\mathrm{g/cm}^3$. Tuning the muon energy between 0.5 and 10 keV enables one to explore sample depths in the range 5–80 nm.

Since graphite is a poor metal, another possible contribution might arise from the creation and decay of muonium, a hydrogen-like atom formed when the positive muon captures a conduction electron. In general, muonium formation is temperature- and energy-dependent [7]. Nevertheless, we exclude muonium formation since: (a) the muonium fraction is expected to increase with implantation depth, whereas the difference between the signals at 20 and 300 K decrease with implantation depth, and (b) a comparison of the TF oscillating asymmetry with the respective ZF asymmetry shows no considerable muonium formation. Therefore, we conclude that the differences between the LE-μSR ZF signals at 20 and 300 K arise solely from the temperature-dependent magnetism of HOPG.

As is evident from Fig. 2, in the interval $2.5 < E_{\mu^+} < 5$ keV, the difference between the LE-μSR signals at the two measured

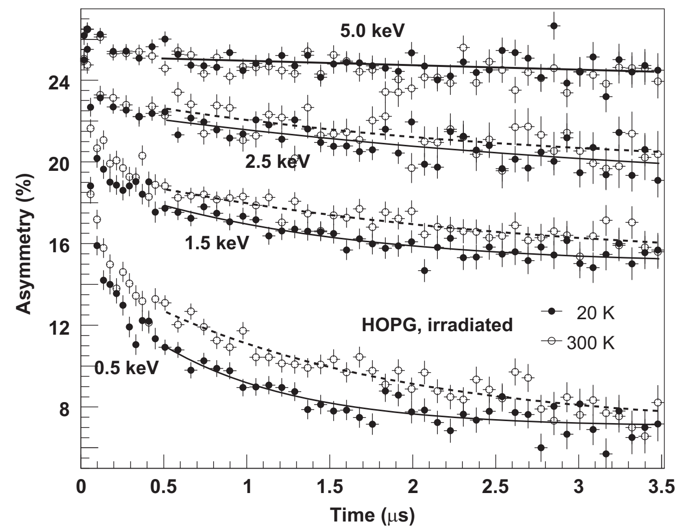


**Fig. 2.** Energy and temperature dependence of the ZF-muon asymmetry measured on an irradiated HOPG sample. The lines serve as guide to the eye.

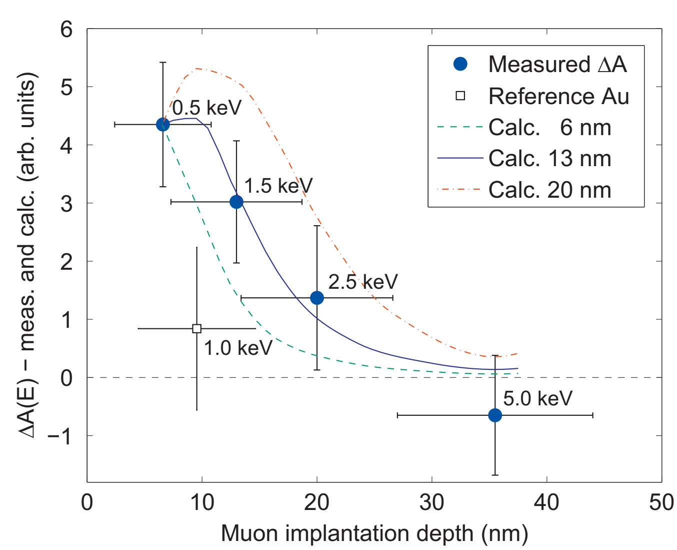


**Fig. 3.** •: Areas enclosed between pairs of LE-μSR spectra of the same energy ($\Delta A$ in Eq. (1)) as a function of the average muon implantation depth. The areas were integrated from the raw signal in the range $0.5 < t < 3.5\,\mu\mathrm{s}$. □: $\Delta A$ from a reference measurement in similar conditions on non-magnetic Au. Lines: Model values of $\Delta A$ (Eq. (1)) for three thicknesses of the magnetic surface layer, $x_0 = 6$, 13, and 20 nm. At each $x_0$ value, $\alpha$ was arbitrarily chosen so that the lowest-energy points coincide.