MUON SPIN ROTATION EVIDENCE OF MAGNETISM IN GRAPHENE

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Introduction

Graphene, a single crystalline layer of carbon atoms, has recently shown extraordinary electronic properties mainly attributed to the two-dimensional and relativistic character of the charge carriers. The possibility that in-plane long range magnetic order could be established in graphene has been theoretically envisaged but not yet experimentally confirmed. We report here the μSR (Muon Spin Rotation/Relaxation) investigation of macroscopic quantities of graphene, prepared by different chemical methods. The observation of muon spin precession in all of these chemically prepared samples gives a clear indication of the presence of long range magnetic order. The magnetic signal appears whenever the graphite planes are separated into layers. Although the muons probe a relatively small local field in the range of 4-8 G, the graphene magnetic order proves to be thermally stable: at 600 K only 40% reduction of local magnetization is observed. The magnetic volume fraction is sample dependent and acquires up to 15% of the sample. A clear correlation between the magnetic signal amplitude and the defect concentration estimated by Raman and SQUID magnetometry suggests that the in-plane defects could be the origin of the magnetic phase. SQUID magnetometry and the measured dependence of local field on an externally applied magnetic field suggest that the magnetic order is of antiferromagnetic type.

Experimental

The measured samples were synthesized in different ways. Sample **1** was prepared following a solvothermal method, as described in detail in [1]. Sample **2** was obtained by thermally annealing Sample **1** at 1073 K for 20 hours under 10^{-6} Torr dynamic vacuum. Sample **3** was prepared starting from highly pure natural graphite powder (SGL Carbon, RW-A grade, average size 66 μm). The partially reduced graphite oxide (GO) was rapidly treated at 673 K in order to obtain the exfoliation of the graphene planes. Sample **4** was obtained by exfoliating preliminarly dried GO at 1323 K for 2 minutes under vacuum. Sample **5** was synthesized as Sample **3** using synthetic graphite fine powder (Aldrich, 99% purity, average size 1.5 μ). Sample **6** was obtained by thermally annealing Sample **5** at 1073 K for 20 hours under 10^{-6} Torr dynamic vacuum.

The muon spin rotation experiments were carried out using the MUSR and EMU spectrometers at the ISIS Facility, UK. The 100% spin-polarized pulsed beam of this facility is particularly suited for the study of the muon spin evolution at long timescales (~ 15 μs) and for the detection or very low precession frequencies. The graphene samples (average weight 250 mg) were contained in air tight Ti cells with thin Ti windows allowing muons implantation. They were filled inside a glove box and, after various thermal treatments, the graphene samples were never exposed to air.

Raman spectroscopy was conducted using a 514 nm green laser inVia Raman Spectrometer with 4 cm^{-1} resolution (10% laser power).

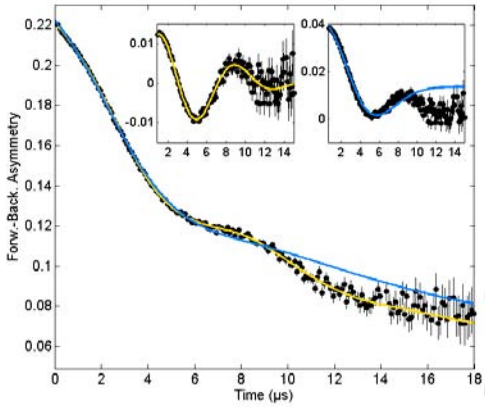

Fig. 1 ZF-μSR evolution of the muon polarization of sample **2** (see table 1). The best fit with a damped oscillation

Results and Discussion

Figure 1 shows the observed time dependence of the muon spin polarization P(t) of a graphene sample. The yellow line shows the fit of the experimental data with the function:

$$P(t) = f_1\left(\frac{2}{3}\cos(\omega_0 t)\exp(-\sigma^2 t^2) + \frac{1}{3}\right) + f_2\exp(-\lambda t) + f_{bg}$$

Two contributions are clearly visible: the first being a precession signal originating from a static local field $H_{loc} = \nu_0/\gamma_\mu = 7.0(2)$ G ($\nu_0 = \omega_0/2\pi$ is the muon precession frequency and $\gamma_\mu = 13.55$ kHz/G is its gyromagnetic ratio), and the second a Lorentzian decaying signal. While the latter (with an amplitude $f_2 = 0.85$, i.e. 85% of the muons implanted in the sample) is induced by fast fluctuating local fields, the former clearly demonstrates that 15% of the sample volume has developed a long range magnetically ordered phase. Several muon decay functions have been tested and excluded before assigning the free precession as the best fitting function. In particular, the most likely alternative candidate would be a Kubo-Toyabe (K-T)[2] depolarization of the muon spin which is expected in the presence of a disordered distribution of static fields. Figure 1 reports the comparison of the fit of our data with two different models: a) a K-T decay function plus a Lorentzian decaying background (blue line, inset on the right), b) free precession of the muon spin plus a Lorentzian decaying background (yellow line, inset on the left). It is evident that the K-T function does not properly fit our data at elapsed times larger than 6 μs. In order to determine if the origin of the

magnetic phase was dependent on the features associated to the specific preparation procedure of the graphene sample (solvothermal synthesis in this case [1]) or an intrinsic property of graphene, we extended the investigation to seven samples prepared in different ways, described in Table 1. The data summarised in the table clearly shows that whenever graphite is exfoliated into single layers, magnetism (which is apparent from coherent muon precession) appears with a sample dependent local field amplitude and volume fraction.

Table 1. μSR results of the different investigated graphene samples

Sample #	μSR precession: local field (G)	Precession fraction f_1 (%)	Lorentz. decay (μs^{-1})	Decaying fraction f_2 (%)
1	8.1(2) (100K)	11.4	0.224(6)	88.6
2	7.0(3)	14.1	0.077(3)	85.9
3	4(1.6)	7.9	0.033(2)	92.1
4	5.5(9)	7.9	0.042(4)	92.1
5	4(2.5)	5.1	0.032(4)	94.9
6	4.5(3) (200K)	4.7	0.019(3)	95.3
7	6(1)	5.9	0.029(3)	94.1

Several theoretical investigations have provided evidence that magnetism in graphene can originate from the zig-zag edge localized states [3] as well as from point defects such as vacancies and chemisorbed hydrogen [4, 5]. Raman spectroscopy was then used to probe the concentration of structural defects in the different samples: the intensity ratio (I_G/I_D) of the observed Raman G and D bands is known to reflect to the amount of in-plane defects in graphene (vacancies and edge sites)[6]. As shown in Figure 2b this ratio clearly correlates with the local field strength of the magnetic phase, as evidenced by μSR. This observation strongly suggests that the origin of the long range ordered magnetic phase detected by μSR could be assigned to the presence of defects in the graphene layer. To further confirm this hypothesis we carried out first-principles calculations of the Fermi contact hyperfine fields on muon spins for different concentrations of defects[7]. The extrapolation to the low defect concentration of the fitted dependence is shown in Figure 2b (dashed line).

The temperature stability of this magnetic phase is clearly exceptional and its transition temperature (TC) is far above room temperature, as shown in Figure 2a. The μSR frequency, which is proportional to the local magnetisation, at 600 K is only reduced to 2/3 of its low T value. This indicates that T_C is most likely far greater than 600 K. μSR is however unable to follow the entire T evolution of the magnetic signal as the amplitude of the precession signal is observed to decrease at increasing temperatures, due to the expected thermal detachment of the Mu from the graphene plane, behaviour similar to what is expected for chemisorbed hydrogen [8].

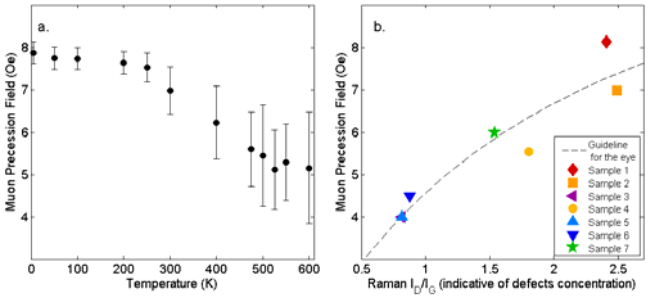

Fig. 2. a. Temperature evolution of the muon precession field (sample **2**), proportional to the local magnetization. **b.** Dependence of the muon precession field on the Raman I_D/I_G bands ratio, indicative of the defects concentration.

Conclusions

In summary we have demonstrated that ZF-μSR has probed the presence of long range magnetic order in graphene. The onset of the magnetism is closely related with the presence of structural defects in the layer, in particular single atom vacancies, and with the exfoliation into single layers. The transition temperature T_C is expected to be much greater than 600 K, at which the local magnetisation is only reduced to 2/3 of its low temperature value.

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References

[1] Choucair M, Thordarson P, and Stride JA, Gram-scale production of graphene based on solvothermal synthesis and sonication. Nat. Nanotechnol. 2009;4:30.
[2] Cox SFJ, Implanted muon studies in condensed matter science. Journal of Physics C: Solid State Physics 1987;20:3187.
[3] Yazyev OV and Katsnelson MI, Magnetic Correlations at Graphene Edges: Basis for Novel Spintronics Devices. Phys. Rev. Lett. 2008;100:047209.
[4] Lehtinen PO, Foster AS, Ma Y, et al., Irradiation-Induced Magnetism in Graphite: A Density Functional Study. Phys. Rev. Lett. 2004;93:187202.
[5] Yazyev OV and Helm L, Defect-Induced magnetism in graphene. Phys. Rev. B 2007;75:125408.
[6] Ferrari AC, Meyer JC, Scardaci V, et al., Raman Spectrum of Graphene and Graphene Layers. Phys. Rev. Lett. 2006;97:187401.
[7] Pereira VM, Guinea F, dos Santos JMBL, et al., Disorder Induced Localized States in Graphene. Phys. Rev. Lett. 2006;96:036801.
[8] Elias DC, Nair RR, Mohiuddin TMG, et al., Control of Graphene's Properties by Reversible Hydrogenation: Evidence for Graphane. Science 2009;323:610.