MuSR STUDY OF HYDROGEN INTERACTIONS WITH DEFECTIVE GRAPHENE

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The unique electronic structure of graphene showing linear band dispersion at the Fermi level, is mainly responsible for the novel fascinating physical phenomena observed in this material [1]. However other graphene singular features could make it quite useful for applications. It possesses, for example, the record surface/weight ratio of 2600 m^2/g thanks to its single atom thickness, which makes it an ideal system for gas adsorption. In particular, the storage of large amount of hydrogen in solid materials is one of the most urgent requests of transportation industry. The development of long range magnetic ordering, possibly triggered by the presence of defects, as theoretically anticipated [2], is another peculiar feature of graphene with evident potential applications in spintronics. Both the interaction of hydrogen with graphene and the onset of magnetism can be properly investigated by the use of a local spin probe like polarized muons. In a Muon Spin Rotation (μSR) experiment, the spin evolution of polarised positive muons implanted in the sample is detected due to the parity violating decay of muons into positrons, which are emitted preferentially in the direction of the muon spin [3]. In particular, in systems with a relatively small electron density like graphene, the implanted muons capture an electron and form muonium (Mu), a light isotope of hydrogen with similar chemical behaviour [4]. Although, due to the typical mm range of muons stopping length, μSR is more suitable for studying massive samples rather than single atomic layers, the recent development of various chemical methods for large scale production of graphene [5] made the present study feasible. Chemically produced graphene is however less 'ideal' than the one obtained by mechanical exfoliation of HOPG as different concentration of in plane defects, mainly vacancies, are known to be invariably produced by the chemical treatments.

In this work we present the μSR study of various chemically prepared graphene samples possessing different concentration of defects. In all the investigated samples a clear oscillation in the time dependence of the muon polarization is observed as shown in Figure 1. More in detail, two components of the muon spin evolution can be singled out: a Lorentzian decay of the spin polarization (dashed line in Figure 1) related to approx. 80% of the implanted muons and a precessing 20% fraction. The latter, which is missing in graphite, where just a slow Korringa-like depolarization is observed[4], originates from a quasistatic local magnetic field at the muon stopping site (approx. 5 Oe in our case), typical of long range magnetism, but might also be due to the dipolar interaction of the muon with a magnetic nucleus, usually H or F [6]. The observation that: 1- the treatment of samples with molecular hydrogen at moderately high temperatures (800C) induces a relevant increase of the precession signal amplitude, and 2- the signal disappears if the treatment is made with deuterium, indicates that its origin is dipolar and not hyperfine. The analysis of the muon spin precession under the hypothesis of the formation of a Mu-H entangled state suggests an inter-nuclear distance of 1.75 Å, fully compatible with a CHMu group. This witnesses an exceptional capture efficiency of mono-hydrogenated defects of graphene for atomic hydrogen (muonium in our case), to form an highly stable di-hydrogenated defect whose structure is shown in Figure 2. The exceptional stability of this moiety is confirmed by the persistence of the precession signal up to 900C [7].

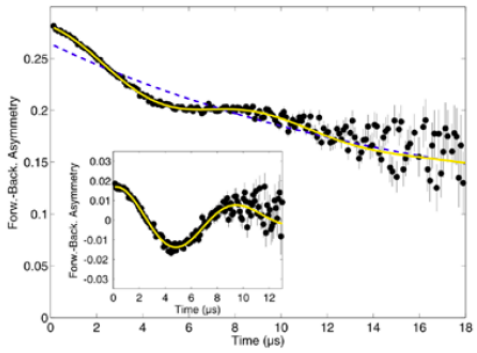

Figure 1: ZF-μSR evolution of the muon polarization in a graphene sample. The solid yellow line is the fit of the data to a precession component (shown in the inset) plus a decaying one (dashed line).

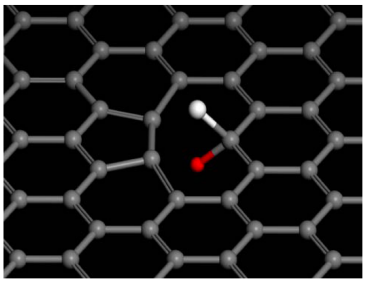

Figure 2: -CHMu defect formed by the Muonium capture by an hydrogenated carbon vacancy.

References

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