A μSR study of single-walled carbon nanotubes

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Abstract

We report μSR experiments on single-walled carbon nanotubes (SWnT). We find that injected muons form vacuum-like muonium (Mu) with a large probability (∼40%). We discuss the temperature (T) dependence of the transverse field (TF) signal of the diamagnetic fraction as well as the longitudinal field (LF) signal of Mu. © 2000 Elsevier Science B.V. All rights reserved.

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SWnT are extremely one-dimensional systems, with diameters on the order of 13 Å, and lengths extending to microns [1]. They consist of graphene sheets wrapped into cylinders having certain well-defined chiralities. In the independent electron approximation, it was predicted that they would be metallic or semiconducting depending on this chirality [2–4]. However, the Coulomb interaction between electrons, low-dimensional instabilities and intertube couplings (the latter within crystalline SWnT ropes) [5–8], may significantly modify the predicted electronic properties. Resulting deviations from simple metallic behaviour may yield, for example, an NMR spin-lattice relaxation rate (1/T1) which does not follow the Korringa Law, as has been observed in low-dimensional organic metals (see Ref. [9] and references therein). It is thus interesting to determine the metallic character of such materials experimentally. While it was initially believed that bulk quantities of predominantly achiral SWnT could be produced [1], it was later found that such samples contained a distribution of chiralities [10]. Moreover, to date, all macroscopic samples are polycrystalline powders, which may contain various residual impurities. Thus there was considerable ambiguity in the interpretation of the results of traditional bulk probes of metallicity, e.g. AC and DC conductivity [11–13]. From the apparently universal occurrence of vacuum-like endohedral muonium in C60 based compounds (e.g. Ref. [14]), we anticipated finding Mu in SWnT, and potentially using its longitudinal field relaxation, analogous to 1/T1, to search for evidence of metallic behaviour. At about the same time,

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though, the techniques of nanophysics were applied to the same samples. Using scanning tunnelling microscopy, the electronic properties could be probed tube by tube, and the results confirmed the gross features predicted by the simplest theories [16] together with some more exotic effects [17]. In addition, atomic resolution images indicated a broad distribution of chiralities [16]. The polychirality of our samples precludes facile conclusions from µSR regarding the metallicity of a fraction of the tubes. Nonetheless our results are interesting in that they indicate the behaviour of muons at an intermediate stage in the continuum of graphitic materials between the highly curved closed shell fullerenes and planar graphite. Furthermore, the behaviour of atomic hydrogen (or its analog Mu) is of some interest in this context as SWₙT and other graphitic materials are important candidates for H storage applications (e.g. Ref. [18]).

We have performed µSR experiments at TRIUMF on two samples of annealed single-walled carbon nanotube ropes in the form of fibrous powders. The first sample (SM11), weighing 80 mg, was wrapped in thin X-ray mylar and mounted in a low background spectrometer [19], and only TF measurements were made. The second, newer and purer sample (SM20), weighing 150 mg, was mounted in a special spectrometer, which allowed us to simultaneously perform a control experiment on high purity Ag at each temperature and field [20], for further results in graphite see Refs. [21,22] and both LF and TF experiments were accomplished.

The SWₙT were formed by laser ablation of graphite in low-pressure He and in the presence of metallic catalysts Ni and/or Co. The as-grown tubes coexist with fullerenes, such as C₆₀ and C₇₀, as well as small particles of the catalysts. A variety of purification procedures effectively eliminate these impurities [23].

In Fig. 1, we give examples of both TF and LF data on SM20. The high TF spectra were fit using a single exponentially relaxing signal. It is immediately obvious that there is a large missing fraction at all temperatures investigated. The T dependence of the diamagnetic fraction is very similar for both samples, and is shown in Fig. 2a. The fit shown for the diamagnetic fraction f_{DIA}(T) in SM20 is

\[ 61.3(8)\% + 33.5(5) \cdot 10^{-4}T - 13.5(1.2)\% (1 - \exp (-8.5(2.0)/T)), \]

Fig. 1. (a) Asymmetry spectra in TF (1.44 T) in the rotating reference frame (195.4 MHz) at 6 K for the silver reference (circles) and the SWₙT sample SM20 (stars). The fits shown give, respectively, asymmetries of: 0.286(1) and 0.132(1) and relaxation rates of: 0.046(2) (Gaussian) and 0.46(2) (exponential) μs⁻¹. (b) An example of the repolarization of a slowly relaxing Mu signal in LF in SM20 at 5 K, for B = 0.01 (circles), 0.1 (triangles), 0.3 (stars) T.

This will be used subsequently in the LF analysis. We note that the energy scale extracted from this dependence is in the range of some energy gaps predicted in SWₙT [5–8], but it could also correspond to the energy required to ionize muonium. The missing asymmetry suggests a large Mu fraction, which is confirmed below in LF. Also shown in Fig. 2 is the T dependence of the TF relaxation rate λ which is larger for the purer sample, indicating that it is not related to residual magnetic catalyst particles. It may be partially due to a broad distribution of muon Knight shifts originating in the distribution of tube chiralities, but

\footnote{Diamagnetic in this sense means simply that there is on average no unpaired electron spin density at the muon.}
a large field-independent contribution to \( \lambda \) indicates that there is another mechanism, likely dynamic charge cycling – rapid capture and loss of electrons by the \( \mu \). There is no evidence of a magnetic transition in the explored \( T \) range, which would give rise to a sharp feature in \( \lambda(T) \). We note that the average shift of the TF precession, using the in situ Ag reference spectra, is small, i.e. less than 100 ppm, and not very \( T \) dependent, behaviour typical of muons in a metal and in contrast to graphite [20–22].

The LF data shown in Fig. 1 indicate repolarization characteristic of Mu. The LF signal is composed of 2 or 3 components. One is a small fast-relaxing signal corresponding to about 10% of the muons. This signal appears to be diamagnetic as its amplitude is independent of field, except at very low field, where it increases slightly. The second is a rather large Mu signal, whose amplitude we infer from fits to the repolarization in Fig. 3. This signal appears to be slowly relaxing, and its amplitude decreases with \( T \) as one would expect from the amplitude of the diamagnetic fraction (Fig. 2a). The third is the LF signal of the diamagnetic fraction, which we assume to be non-relaxing in LF.

We first fit the field dependence of the LF spectra using two signals, with the amplitude of the fast relaxing component fixed independent of field. In addition we used the behaviour of the silver reference spectra to estimate the effect on the LF asymmetry baseline due to positron steering by the magnetic field. This was done by simply scaling the field dependence of the reference baseline, which gave reasonable results except above 1 T.\(^3\) The field

\(^3\)This indicates that at high fields the field dependence of the effective solid angle of the positron counters is not exactly the same for the different geometries of the sample and reference: the Ag reference is an annulus around the sample.
dependence of the slowly relaxing asymmetry (Fig. 3) is fit to a (single component) isotropic Mu form, i.e. $A_0 + A_{\mu_0}(1 + 2x^2)/(2 + 2x^2)$, where $x$ is the reduced field, $x = \frac{\tilde{A}}{\gamma_e + \gamma_\mu}$, and $\tilde{A}$ is the hyperfine parameter and $\gamma_\mu$ are the respective gyromagnetic ratios of the electron and muon. $A_0$ here represents the asymmetry of the diamagnetic fraction. From the fits, the values of the hyperfine parameter is vacuum-like, i.e. 4200(260) MHz at 5 K and 4410(500) MHz at 60 K, where the errors are only statistical. There is insufficient data at 275 K for a reliable fit, so the curve in Fig. 3 has $\tilde{A}$ fixed at the 60 K value. Note the 20 G point at 275 K suggests there may also be some low field decoupling.

The relaxation rate of the slowly relaxing component is too low to determine independently of its amplitude. To make a reasonable estimate of its magnitude and T dependence, we must therefore include the observed $T$ dependence of the amplitude. To do so, we assume the Mu fraction has the form $1 - f_{\text{DIA}}(T)$ where $f_{\text{DIA}}$ is the diamagnetic fraction from Fig. 2. The amplitude of the fast-relaxing component, when free, was found to be essentially independent of $T$, so it was fixed to its average value. The subsequent 3 component fits (including the non-relaxing signal) yielded the relaxation rates shown in Fig. 4. Both rates follow approximately the same $T$ dependence, and appear to have a peak near 150 K. The origin of this $T$ dependence is not yet clear. However, the similarity of the $T$ dependence suggests an intrinsic relaxation mechanism (possibly connected with the charge cycling rate) because one would not expect, for example, relaxation from diffusion of vacuum-like Mu to have the same $T$ dependence as the relaxation of other muon states. In fact the peak coincides with the crossover $T$ between the bulk high-$T$ metallic resistivity and low-$T$ semiconducting regimes of similar samples [11–13]. It will be very interesting to compare our $1/T_1(T)$ with results from NMR when they become available.

In conclusion, we have established that a large fraction of muons stopped in SWnT form muonium, a result which disagrees with measurements in very early samples of multiwalled tubes [24]. Mu formation may correspond to a large fraction of semiconducting tubes, or it may be independent of metallicity, as it is in C$_{60}$ compounds. There are interesting $T$ dependences in both the LF and TF data, but we cannot, at this stage, attribute them to specific electronic properties of the SWnT.

References