^{13}C NMR and EPR of carbon nanofoam

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The ^{13}C NMR spectra of a carbon nanofoam sample, exhibiting a peak in the ZFC magnetic susceptibility, show a single ^{13}C line at room temperature and a two peak structure at 100 K. The splitting and the NMR shifts are however much too small to be associated with true ferromagnetism as for instance observed in TDAE-C$_{60}$ below T_C. The X-band EPR spectra show the presence of a least three different paramagnetic clusters with $g_a = 2.0016$, $g_b = 2.0031$, $g_c = 2.0036$ and very different electronic spin–lattice relaxation times. In some samples the CW EPR spectra show an additional rather broad and strongly temperature dependent line shifted to lower fields, which is characteristic of ferromagnetic systems. The results thus show an inhomogeneous super-paramagnetic or spin-glass like nature of magnetism in cluster assembled carbon nanofoam rather than homogeneous ferromagnetism.

1 Introduction

Ferromagnetism is typically the property of transition metals with unpaired electrons in unfilled atomic shells. Nevertheless various forms of carbon systems have recently been found [1–6] to exhibit ferromagnetic or ferromagnetic like behaviour. This is true for the purely organic ferromagnet TDAE$^+$-C$_{60}^-$ [1], polymerized C$_{60}$ [2–4], hydrogenated amorphous carbon [5] as well as cluster assembled carbon nanofoam [6]. This system which has an ultra-low density, $2–10$ mg/cm^3, and a large surface area of $300–400$ m^2/g is obtained by laser ablation of glassy carbon in an argon atmosphere [6]. Electron diffractions suggest [7] the presence of hyperbolic "schwarzite" layers. A weak ferromagnetic like hysteresis curve has been observed in this system with a saturation magnetization of about 0.3 emu/g. A much larger saturation magnetization was seen immediately after formation. Some samples show a maximum in the magnetic susceptibility between 50 K and 100 K characteristic of spin glasses. In addition they show a large difference between field cooled (FC) and zero field cooled (ZFC) magnetic susceptibilities which also indicates spin-glass like or superparamagnetic behaviour. The aim of this contribution is to check the nature of the magnetic state in carbon nanofoam on an atomic level via ^{13}C NMR and EPR.

2 Experimental

Cluster assembled carbon nanofoam was prepared from glassy carbon by laser ablation in an argon atmosphere with $p = 2$ Torr, 50 Torr and 200 Torr. Fourier transform solid-state spin-echo ^{13}C NMR spectra were measured at a Larmor frequency $\nu_L = 95.572$ MHz. A high-resolution magic angle sample spin-

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ning (MAS) ^{13}C NMR spectrum at room temperature was measured at a commercial Bruker spectrometer at $\nu_L = 150.842$ MHz. The sample rotation frequency was 20 kHz. The EPR spectra and electron spin−lattice relaxation were measured on an X-band Bruker EPR spectrometer allowing pulsed and CW operation. The magnetic susceptibilities were measured between 4 K and 300 K on a squid magnetometer in a magnetic field of 100 Oe.

3 Results and discussion

The high-resolution ^{13}C NMR MAS spectrum of carbon nanofoam prepared in the Ar atmosphere with $p = 50$ Torr is shown in Fig. 1. It consists of three components shifted for 28, 140 and 174 ppm with respect to TMS. The relative intensities of these components are 15, 31 and 139. The width of the spectrum shows that we deal with a distribution of the isotropic ^{13}C chemical shifts. The spectrum is somewhat similar to the one of hydrogenated amorphous carbon [8], where lines at 35 and 124 ppm were found as well as a broad shoulder at 160 ppm. The low-shift component can be assigned to sp^3 hybridized carbons whereas the high-shift components are due to the dominant sp^2 hybridized carbons. The relatively small differences in the shift values may reflect the curved structure of carbon nanofoam.

The wide-line ^{13}C NMR spectra taken at room temperature and at 100 K are compared in Fig. 2. The linewidth at room temperature is here about 20 kHz. The ^{13}C spin−lattice relaxation time is of the order of a few ms and is clearly determined by paramagnetic electron-nuclear interactions. The two peak structure at 100 K shows the presence of magnetically nonequivalent carbon sites. The separation between the two peaks is too large to be explained by different sp^2 and sp^3 electronic carbon configurations. The observed linewidth and NMR shifts are however much too small to be compatible with ferromagnetic behaviour as observed for instance in TDAE-C_{60} [1]. They rather indicate superparamagnetic behaviour. The inhomogeneous nature of the sample is also reflected in the rather short T_2 values. We thus deal with frequency distributions rather than with single lines. This also speaks in favour of the superparamagnetic nature of the sample, again in an analogy with amorphous hydrogenated carbon [8].

It should be stressed that the measurements are extremely time consuming in view of the extremely low density of the sample and the small natural abundance of ^{13}C. About 900 000 repetitions had to be made to get a good signal-to-noise ratio.

To have a further check on the proposed superparamagnetic nature of carbon nanofoam we decided also to look at the magnetic susceptibility and the electron paramagnetic resonance (EPR) spectra.
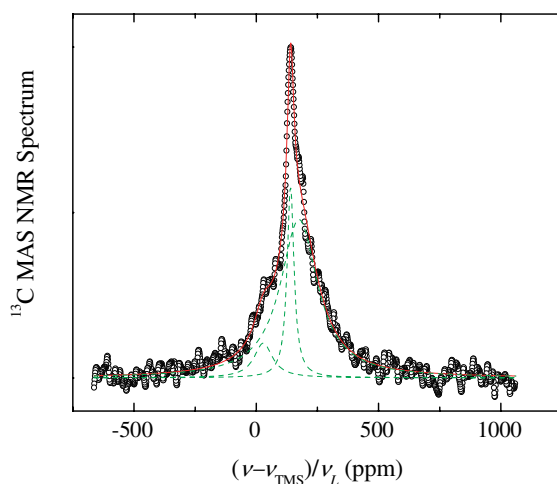

Fig. 1 (online colour at: www.pss-b.com) MAS ^{13}C NMR spectrum of carbon nanofoam at room temperature (circles). The solid line is the sum of thee components (dashed lines), into which the spectrum can be decomposed.
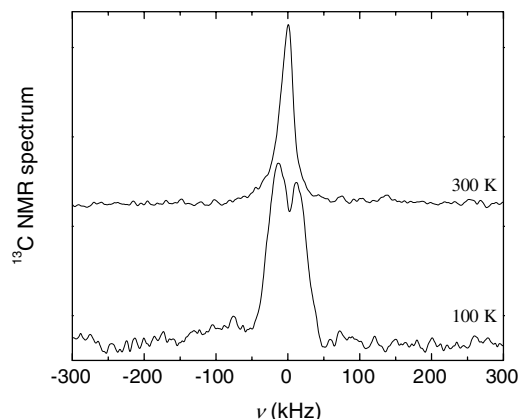
Fig. 2 ^{13}C NMR spectra of carbon nanofoam (p = 50 Torr) at room T and at 100 K.

The temperature dependence of the FC and ZFC magnetic susceptibilities of carbon nanofoam samples prepared in an Ar atmosphere with p = 2 Torr, 50 Torr and 200 Torr are shown in Fig. 3. They all show an increase in the FC susceptibilities at low temperatures and a large difference between the FC and ZFC values, characteristic for supeparamagnetic or spin-glass systems. The sample prepared in an atmosphere with p = 50 Torr in addition shows a spin-glass like peak in the ZFC susceptibility between 50 K and 100 K.

The pulsed X-band EPR spectra obtained by the field swept echo technique [Fig. 4] and by Furier transform of the free induction decay signal show the presence of at least three different paramagnetic centers with different g-factors and electronic spin−lattice relaxation times:

(a) a center with g_a = 2.0016 and a rather long $T_{1a} \approx 1$ ms,
(b) the main center with g_b = 2.0031 and a very short $T_{1b} \approx 100$ ns,
(c) a center with g_c = 2.0036 and $T_{1c} \approx 0.1 - 1$ µs.

The higher g-factors are typical of amorphous carbon systems with significant sp^3 character arising from non-planar parts of the carbon sheets. The g = 2.0036 center rapidly disappears above 80 K, i.e. above the susceptibility maximum. No non-carbon paramagnetic impurities were found. The g = 2.0016 line is not present in samples prepared at high Ar pressures.
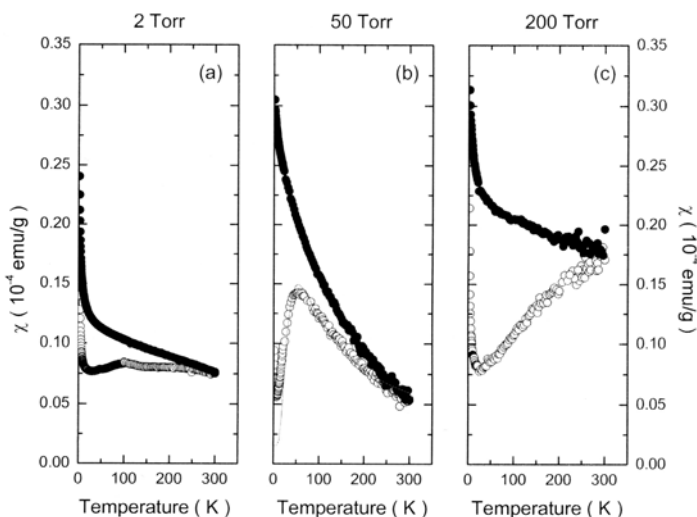

Fig. 3 Zero field cooled (open circles) and field cooled (solid circles) magnetic susceptibilities of cluster assembled carbon nanofoams obtained in different Ar atmospheres.
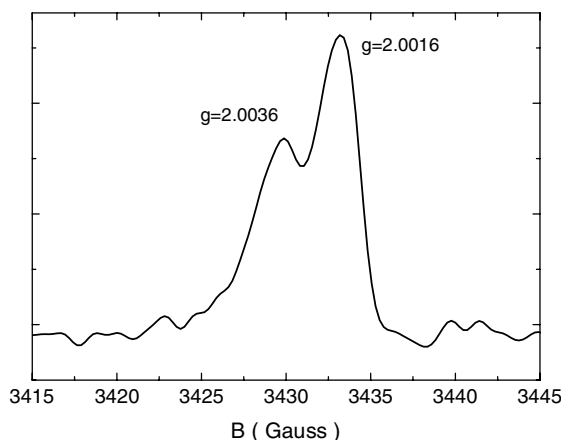
Fig. 4 X-band field swept echo EPR spectrum of paramagnetic center in carbon nanofoams.
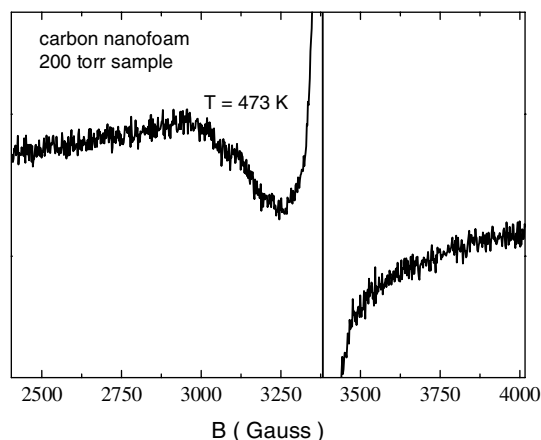
Fig. 5 CW X-band EPR spectrum of carbon nanofoam showing a broad T-dependent ferromagnetic like line shifted to lower fields in addition to the sharp $g = 2$ paramagnetic line. The broad line is seen only in some and not in all samples.

The CW EPR line shape strongly deviates from a simple Lorentzian line shape. In some samples an additional broad strongly temperature dependent EPR line shifted to lower fields by 400 Gauss at room temperatures, has been observed (Fig. 5). On heating from 300 K to 600 K the shift of this line dereases from 400 G to 150 G with respect to the position of the $g = 2.0032$ narrow line. Such temperature dependent broad lines are characteristic of superparamagnetic and ferromagnetic-like systems. It should be noted that there is some adsorbed hydrogen at the nanofoams. The adsorbed hydrogen shows at room temperature a two component proton NMR magnetization decay in the ms range with $T_{1a} \ll T_{1b}$.

The above results demonstrate the magnetically heterogeneous nature of carbon nanofoam with spin correlated magnetic clusters embedded in a non-spin correlated medium. The results thus show that carbon nanofoam is an inhomogeneous spin-glass like or superparamagnetic material with a high spin blocking temperature rather than a true homogeneous ferromagnet.

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