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Magnetic properties and phase transitions of gadolinium-infused carbon nanotubes

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Carbon nanotube (CNT)/metal-cluster-based composites are envisioned as new materials that possess unique electronic properties which may be utilized in a variety of future applications. Superparamagnetic behavior was reported for CNTs with Gd ions introduced into the CNT openings by internal loading with an aqueous GdCl₃ chemical process. In the current work, the magnetic properties of the CNT/Gd composites were obtained by the joining and annealing of Gd metal and CNTs at 850 °C for 48 h. Energy dispersive X-ray analysis shows the presence of Gd intermingled with the CNT walls with maximum and average Gd concentrations of about 20% and 4% (by weight), respectively. The Gd clusters have a non-uniform distribution and are mostly concentrated at the ends of the CNTs. A ferromagnetic-type transition at $T_C \sim 320$ K, accompanied by jump like change in magnetization and temperature hysteresis typical for the temperature induced first order phase transitions has been observed by magnetization measurements. It was found that Gd infused into the CNTs by the annealing results in a first order paramagnetic-ferromagnetic transition at $T_C = 320$ K. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4796151>]

I. INTRODUCTION

Nanocomposite magnetic materials have the advantage of acquiring singular magnetic properties that are not normally observed in other materials. These magnetic materials have unlocked a new path of opportunities in the technological and medical disciplines; they have potentially provided new measurement methods and medical procedures that may be utilized in a variety of current and future applications.¹ A new property of materials in which our study finds its background, is the superparamagnetic behavior of carbon nanotubes (CNTs) produced when Gd ions are introduced into the CNT's openings by internal loading with an aqueous GdCl₃ chemical process. These molecular magnets are used as contrast agents in magnetic resonance imaging, and have shown an efficacy 40 to 90 times larger than any other Gd³⁺-based contrast agent.^{2,5,6} The maximum magnetic moment of gadolinium is $7\mu_B$ which is about two times larger than those of the 3d metals Fe, Ni, and Co. Therefore, molecular magnets based on Gd metal are expected to show enhanced magneto-responsive properties relative to those based on 3d-metals. However, the introduction of Gd-based compounds into carbon nanotubes using an aqueous chemical process results in paramagnetic/superparamagnetic behavior of the composites [see Ref. 2 as an example], resulting in a limited range of application that depends on the nature of the magnetic order of the composites. In the current work, the magnetic properties of the CNT/Gd composites were obtained as a result of the joining and annealing of Gd metal (99.9% of purity) and CNTs at 850 °C for 48 h, which is an innovative method to

achieve the discussed outcome of merged Gd atoms into the CNTs by diffusion. The phase transition to a ferromagnetic-like state at about 320 K has been detected for the CNT-Gd composite.

II. EXPERIMENTAL DETAILS

The carbon nanotubes were synthesized by an air-assisted chemical vapor deposition technique³ and detached mechanically from aluminum substrate. To transfer Gd ions into CNTs, we followed the diffusion process. The Gd fragments of 99.99% purity were joined together to form a single ingot under an ultra-high pure argon atmosphere in an arc-melting furnace. Subsequently, the ingot was placed in a diamond saw and cut in half, forming two plates of high purity Gd; the CNTs were placed between the two Gd plates forming a sandwich-like Gd-CNT-Gd structure and annealed under high vacuum ($\approx 10^{-5}$ Torr) for a time period of 48 h at a constant temperature of 850 °C. The Gd-CNT composite was characterized with field emission scanning electron microscopy (FESEM, Quanta FEI 450 D 9506), with elemental analysis capabilities using energy dispersive x-ray analysis (EDAX). The concentration of Gd intermingled within the CNT's walls was determined using the EDAX available in the FESEM. Thermo-magnetic measurements have been performed with a superconducting quantum interference device magnetometer (SQUID, Quantum Design) in the temperature interval (5-400 K) and magnetic fields up to 20 kOe. The magnetization curves $M(T)$ have been measured during the heating and cooling cycles after the sample has been cooled down from 380 K to 5 K at zero magnetic field (zero-field-cooled (ZFC)) and start from 380 K, respectively, at magnetic fields 500 Oe and 20 kOe.

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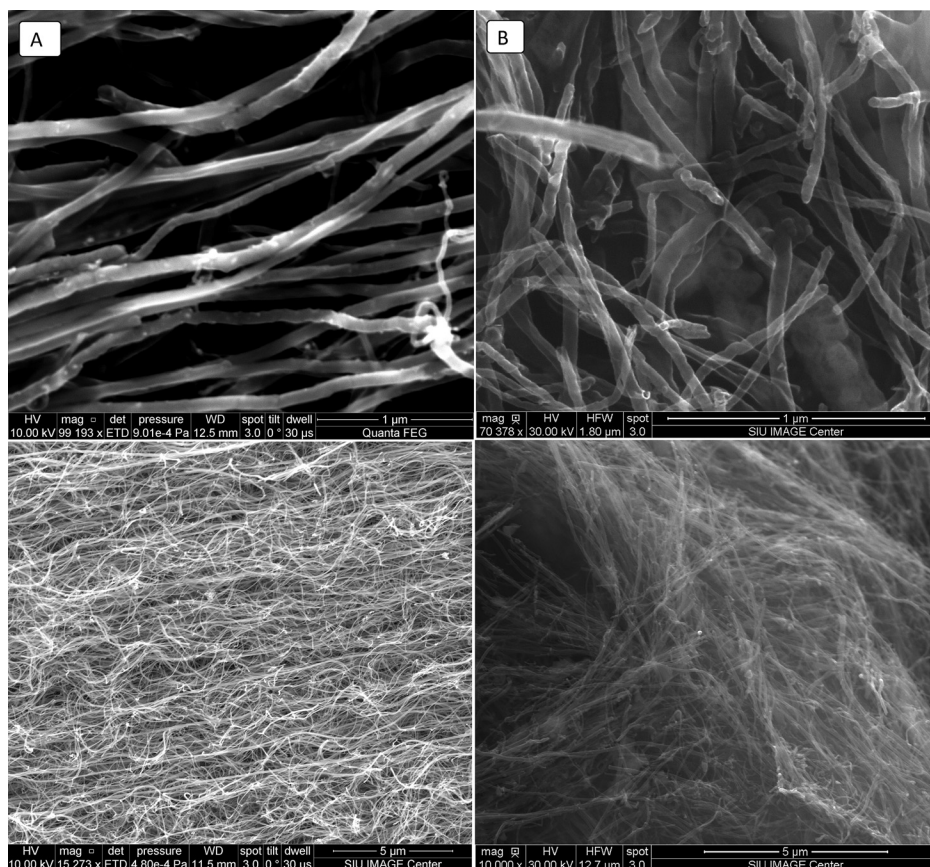


FIG. 1. SEM images of CNT without Gd (a) and CNT+Gd (b).

TABLE I. EDAX elemental analysis at 20 μm .

Element	Wt. %	At. %
C	75.65	83.27
O	19.71	16.29
Cl	0.05	0.02
Fe	0.07	0.02
Cu	0.07	0.01
Zn	0.18	0.04
Ge	0	0
Gd	4.28	0.36
Total	100	

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 illustrates the results from the EDAX measurements for both the parent CNTs and CNT+Gd. The heavy metal (Gd) tends to appear in a brighter color since the microscope electrons scatter from the surface.⁷ Referring to Figure 1(a), one can see that the parent CNTs have a visible uniformity in the colors and brightness since the microscope electrons pass through the CNT's surface without being scattered. On the other hand, in Figure 1(b), the CNTs faintly appear due to the EDAX contrast effect, while the areas where Gd has been absorbed by the CNTs appear more pronounced. EDAX analysis verifies that the CNTs contain Gd.⁴

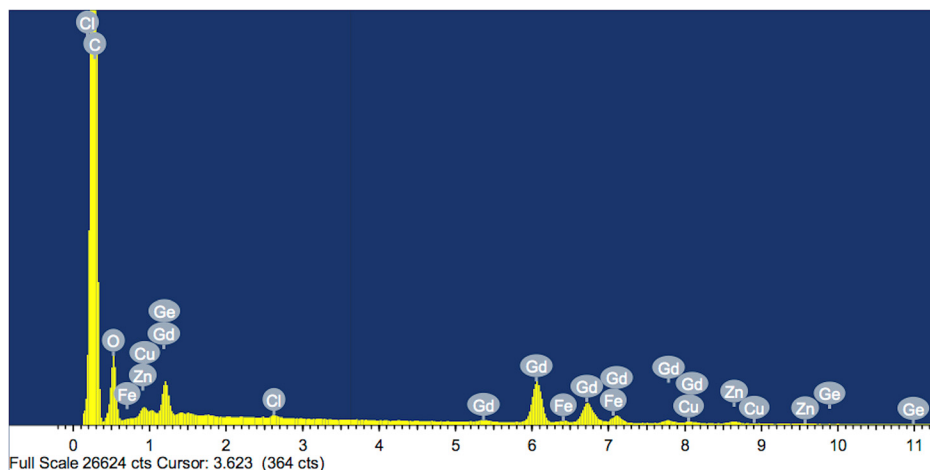


FIG. 2. Example of EDAX microanalysis.

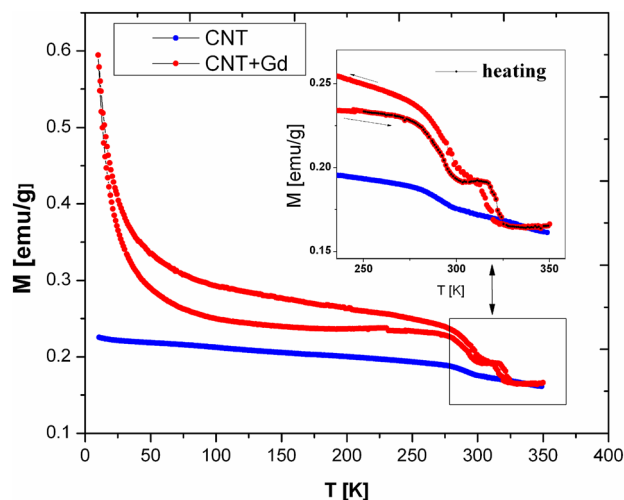
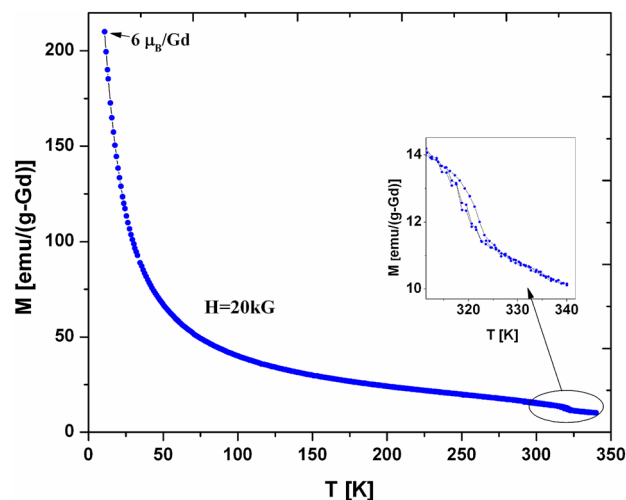


FIG. 3. MvT at 500G for CNT and CNT+Gd.

Results from the EDAX elemental analysis of a $10\ \mu\text{m}$ by $20\ \mu\text{m}$ window show that Gd is 4.3% of the CNT/Gd analyzed sample (see Table I and Figure 2). Therefore, some fraction of Gd atoms has been absorbed by the CNTs, and the Gd atoms basically reside in sites at the tube ends and in defects. These results reflect the similar outcome observed in Ref. 2. As we reduce the dimensions of the window from the EDAX elemental analysis, the percentage of Gd increases, respectively, until it reaches approximately 20% of the total weight of the impregnated CNT.

The results of the magnetization measurements are shown in Figure 3. The $M(T)$ curve of CNT shows smooth change in magnetization with respect to the temperature at about 270 K. In the CNT/Gd sample, the behavior of $M(T)$ shows remarkable changes in the magnetic properties. Two transitions are clearly visible: one at 270 K and another at 325 K for Gd+CNT sample. The high temperature transition shows a jump like decrease in magnetization with increasing temperature and temperature hysteresis of magnetization $M(T)$, typical for temperature-induced first order transition from ferromagnetic to paramagnetic states. From the comparison of the $M(T)$ curves obtained for applied magnetic fields $H = 500\ \text{G}$ and $20\ \text{kG}$ (Figure 4), it is possible to see that $M(T)$ at $20\ \text{kG}$ still shows the jump-like transition at about 320 K with temperature hysteresis. The transition at 280 K is “suppressed” by the magnetic field. The suppression is most likely related to the presence of the small amount of magnetic impurities in the sample. In the region where the sample magnetization is far from saturation and the sample is characterized by a large magnetic susceptibility, the contribution from magnetic impurities to the total magnetization becomes undetectable at high applied magnetic fields. Considering that iron has been used as a catalyst for the growth of the CNT samples, and that CNTs contain only a small amount of iron (0.07 mass %, see Table I), the transition at 280 K most likely related to iron based impurities. The maximum magnetic moment of CNT/Gd at $T = 10\ \text{K}$ in the applied magnetic field $H = 20\ \text{kOe}$ is $6\ \mu_{\text{B}}/\text{Gd}$, as estimated from $M(T)$ (see Figure 4) and Gd concentration (see Table I).

FIG. 4. MvT of CNT-Gd composite obtained at applied magnetic field $H = 20\ \text{kG}$ calculated per Gd atom using the results of EDAX analysis (see Table I).

This value is in good agreement with a magnetic moment of $7\ \mu_{\text{B}}$ for the Gd^{+3} ion.²

IV. CONCLUSION

It has been shown that during the annealing of the sandwich-like Gd-CNT-Gd structure for 48 h, Gd ions can penetrate the CNTs up with maximum and average Gd concentration of about 20% and 4% (by weight), respectively. The presence of Gd in the CNT can modify the magnetic properties of the CNT and result in a first paramagnetic-ferromagnetic phase transition near room temperature. Therefore, the Gd-CNT composite obtained by the diffusion method of synthesis is a prospective material for future investigations in medical and other technological disciplines.

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