

MAGNETIC SEPARATION OF  $GdC_2$  ENCAPSULATED IN  
CARBON NANOPARTICLES

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**Abstract**—Single crystal particles of  $\alpha$ - $GdC_2$  have been encapsulated into carbon polyhedral shells by the carbon arc-discharge technique. These particles range in size from 20 to 50 nm and are paramagnetic in nature. The phase and stoichiometry of these crystals have been determined using a combination of techniques, such as X-ray diffraction and high-resolution electron microscopy. As reported for  $\alpha$ - $LaC_2$  earlier, the crystal structure of bulk  $\alpha$ - $GdC_2$  is also tetragonal, and it is metallic and undergoes hydrolysis. However, the encapsulation of the nanoscale crystals in carbon shells prevents their hydrolysis indefinitely. These nanometer-sized particles, which can be preferentially extracted using powerful magnetic fields, may have useful applications in several fields of science.

**Key Words**—Gadolinium carbide, nanotubes, carbon shells, encapsulation.

The discovery in 1991 by Iijima[1,2] of nested carbon nanotubes and nanopolyhedra as a by-product of fullerene production has sparked a significant amount of interest into the research of these novel forms of carbon. Theoretical calculations[3-8] have shown that these materials would possess unique electrical, thermal, and mechanical properties that could be of value to several diverse fields of science. The successful production of endohedral fullerenes by several researchers[9-12] prompted our first attempt at filling the cavities of the tubes and polyhedra with highly electropositive elements. Our results, reported previously, showed successful encapsulation of single-crystal, nanometer-sized particles of  $\alpha$ - $LaC_2$  into about 50% of the carbon polyhedral shells using arc-discharge conditions that favored the growth of carbon nanotubes and polyhedra[13].

In order to effectively utilize the benefits of such high-density nanoparticles (density of  $\alpha$ - $LaC_2$  is 5.32 gm/cc), it would be desirable to extract them preferentially from the rest of the products of the arc-discharge experiments. Encapsulated materials of a variety of sizes and morphologies are difficult to separate in bulk using either physical or chemical means. Magnetic means of extracting  $\alpha$ - $LaC_2$  particles would not be successful, as they are only weakly diamagnetic. Our initial attempts at encapsu-

lating a ferromagnetic element (Fe) were not successful, and this may be due to several factors, among them the higher ionization potential of Fe compared to that of La, or the lower melting temperature and higher vapor pressures of the carbides of Fe compared to those of  $\alpha$ - $LaC_2$ . In this paper we report the successful encapsulation of Gd, one of the four ferromagnetic elements. The paramagnetic properties of the carbon-shell encapsulated, single crystals of  $\alpha$ - $GdC_2$  are also reported.

Analogous to our production of  $\alpha$ - $LaC_2$  encapsulated in carbon nanoparticles[13], the arc-discharge experiments were run using 7.9-mm-diameter, 30.5-cm-long graphite anodes, which were drilled to a depth of 23 cm with a 3.2-mm drill and packed with either  $Gd_2O_3$ , which has negligible magnetic susceptibility, or pure Gd metal. The carbon arc conditions were a DC current of 75 A, and gap distances of 2-5 mm and 2-8 mm from the 12.7-mm-diameter cathode for the  $Gd_2O_3$  and Gd runs, respectively. The corresponding He pressures were 1,000 Torr ( $Gd_2O_3$ ) and 500 Torr (Gd), and the Gd:C molar ratios were 2.3:100 ( $Gd_2O_3$ ) and 8.2:100 (Gd). Under these conditions a cylindrical boule grows outward from the end of the graphite cathode. The central core section obtained from this cylindrical growth on the end of the cathode was powdered. A sample of the Gd-containing powder (ca. 50 mg)

obtained from the  $Gd_2O_3$ -packed anode case was heated in air in a TGA, and the weight of the residual ash was 31.2%. XRD analysis of the ash showed it to be pure  $Gd_2O_3$ . From these results we calculate the Gd content to be 2.8 at%, which is slightly higher than the original 2.3 at% Gd (present as  $Gd_2O_3$ ) in the anode.

The powders were dispersed in ethanol by sonification, and then deposited on holey carbon-coated Cu grids, and air-dried for characterization by transmission electron microscopy (TEM). Most of the electron microscopy used to study these materials was carried out on a JEOL 2000-FX TEM operated at 200 kV. The Atomic Resolution Microscope at the National Center for Electron Microscopy, Lawrence Berkeley Laboratories, as well as a Philips CM-30 TEM equipped with a Link windowless detector, were also used for high-resolution microscopy and elemental analysis, respectively.

Arc-discharge experiments, run with either a metal or an oxide in the anode, produced significant quantities of carbon nanopolyhedra, with roughly 50% filled or partially filled with gadolinium carbides.

X-ray analysis of the product of the arc-discharge

experiments using pure Gd metal in the anode showed that it consisted of  $GdC_2$ ,  $Gd_2C_3$ , and graphite carbon. The products from the experiments involving  $Gd_2O_3$  are the same, but the relative peak heights were significantly lower in the latter due to the presence of substantial amounts of amorphous material (mostly carbon). The presence of the  $M_2C_3$  species in the product from the arc-discharge experiments using  $Gd_2O_3$  or Gd metal distinguishes it from our previous work on La[13], where only  $\alpha-LaC_2$  was observed.

One potentially interesting aspect is the modification of the density of the nanopolyhedra when they are filled with a high-density material such as  $GdC_2$  (6.94 gm/cc) vs. empty. Filled nanoparticles will have densities that range from 3–5 gm/cc vs. approximately 1.7 to 2 gm/cc. Like  $\alpha-LaC_2$ ,  $\alpha-GdC_2$  is metallic[14], with a resistivity of 55.3  $\Omega$  cm at 273 K.

It was possible to extract a component of the product at room temperature using a strong magnetic field. X-ray analysis of the magnetically extracted material showed a dramatic decrease in the peak heights of the  $Gd_2C_3$  component, relative to the other components. A bright-field image of the

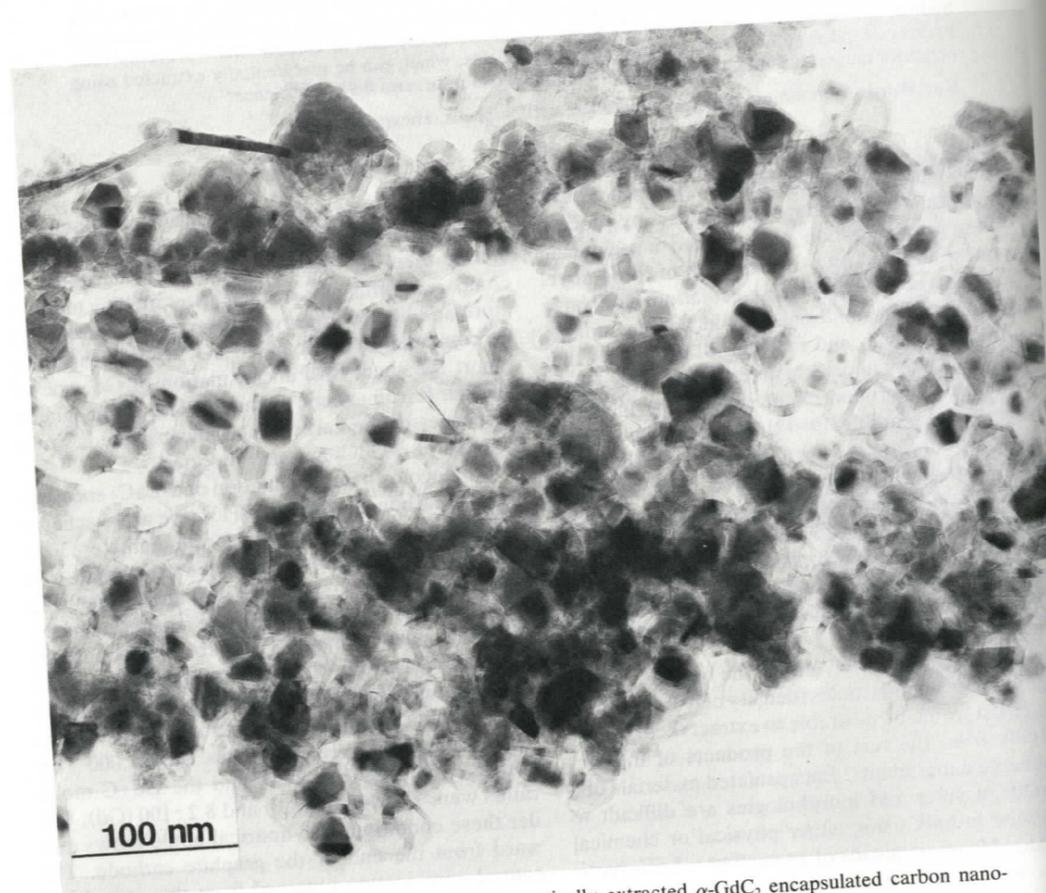


Fig. 1. Bright-field TEM micrograph of magnetically extracted  $\alpha-GdC_2$  encapsulated carbon nanopolyhedra.

magnetically extracted material in Fig. 1 shows that it essentially consists only of encapsulated particles ranging from 20 to 50 nm in size. This implies that the magnetic component is single crystal particles of  $GdC_2$  encapsulated in the nanopolyhedral shells of carbon.

Accurate measurement of the lattice fringe spacings from several high-resolution images of the magnetically extracted nanoparticles showed that the spacings matched well with the interplanar spacings of the (101), (002), and (110) planes of  $\alpha-GdC_2$ . Imaging of higher-index lattice planes was limited by the line resolution of the 2000-FX. Further verification of the phase of the encapsulated particles was obtained by measurement of the angles of different sets of fringes, which matched very well with those from theoretical calculations for tetragonal crystals[15].

Specific magnetic properties of these materials were investigated using a magnetometer (PAR model 4500 VSM) capable of stabilized sample temperatures from 4 to 325 K and magnetic field strengths up to 10,000 Oersted. To accommodate as much material as possible in the VSM probe chamber, the samples were pressed and formed into discs 3 mm diameter by 2 to 3 mm long, consisting typically of 5 to 50 milligrams of material. Random samplings of Gd-carbon materials were collected from core and soot material, and magnetically extracted samples were pulled at room temperature using a 5 kG samarium cobalt magnet.

X-ray diffraction and corresponding magnetization data (insets) are illustrated in Fig. 2 for ran-

domly selected and magnetically extracted core material from a run with gadolinium metal rod packing. The purely paramagnetic character of the two samples is apparent, as is the large difference in the ratio of paramagnetic material per gram mass. The magnetic extraction has resulted in a 20-fold increase in the concentration of the paramagnetic component for this particular sample. Samples taken from subsequent runs under different cell conditions have produced a magnetic component comprising >80% of the central core. All the samples generated with Gd metal or  $Gd_2O_3$ , and obtained from the core material, have exhibited this paramagnetic behavior.

Temperature-dependent magnetic moment data for the Gd-carbide encapsulates over the range 4 to 300 K are shown in Fig. 3. Based upon the XRD analyses, the paramagnetic response of the Gd-carbide sample appears to be the result of gadolinium dicarbide, which in bulk form has an antiferromagnetic transition temperature of 42 K[16]. Since the  $GdC_2$  crystal sizes observed by TEM are on the order of 100 nm or less, and their moments are essentially isolated and uncoupled, a clear antiferromagnetic transition temperature for  $GdC_2$  at 42 K is not observed. For  $GdC_2$  particles of this size, the thermal energy required to overwhelm the energy barrier of stationary moments and flip them in an external field is expected to be relatively small; therefore, the net magnetic moment should follow the Curie law  $1/T$  dependence down through the transition temperature. These encapsulated  $GdC_2$  crystals fulfill this requirement, and are thus consid-

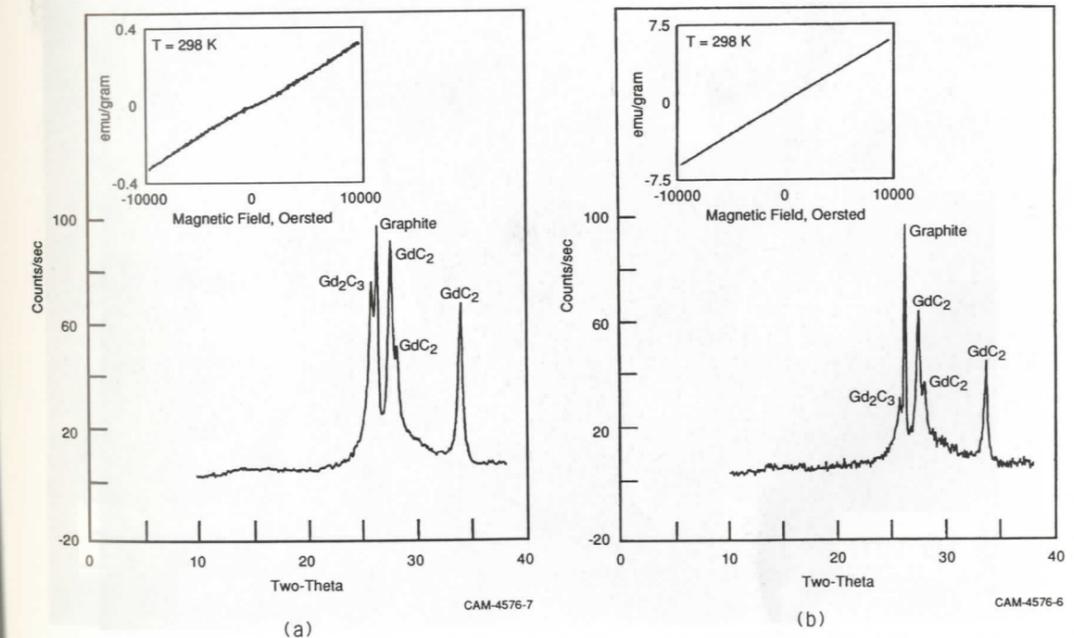


Fig. 2. XRD and magnetization curves (insets) for (a) random and (b) magnetically selected core material.

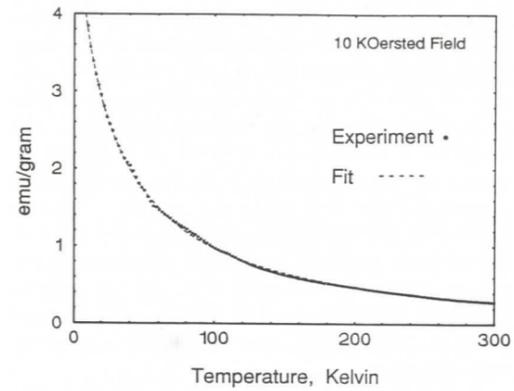


Fig. 3. Moment vs. temperature for Gd-carbon encapsulate sample generated from  $Gd_2O_3$  packing. The fitted curve is a least-squares fit to  $1/T$  Curie law.

ered superparamagnetic[17]. With the exception of variations in magnitude, the magnetization loops and  $M$  vs.  $T$  curves of all raw and extracted core samples appear identical.

Based on the study of high-resolution images obtained from the predominantly amorphous regions of carbon containing a fine dispersion of Gd, as verified by elemental analysis using energy dispersive spectroscopy (EDS), we can speculate on a possible encapsulation mechanism for the  $GdC_2$  nanocrystals in the carbon polyhedral shells. We speculate that the Gd/C amorphous material (with

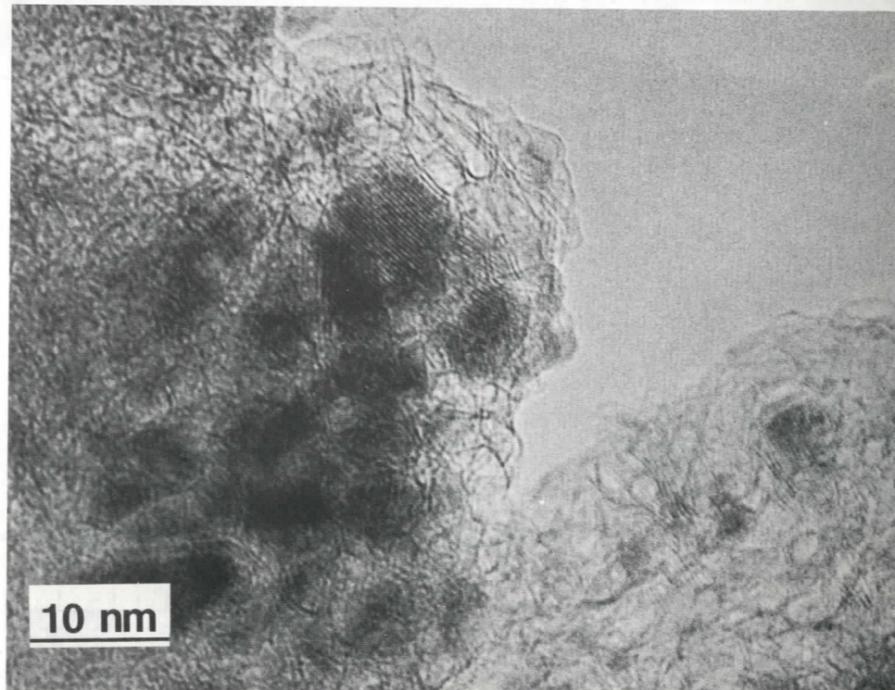


Fig. 4. High-resolution TEM image of Gd/C amorphous component, which appears to suggest that the carbide crystallizes prior to carbon.

only a few atomic percent Gd in carbon), phase segregates into ultrafine aggregates of Gd carbides in a matrix of amorphous carbon. The high-resolution image in Fig. 4 suggests that the carbide may crystallize prior to the carbon shell. Specific planes of the crystallized carbide particles appear to promote the graphitization of the carbon layer planes from the inside out; the high resolution image in Fig. 5 illustrates  $GdC_2$  crystals surrounded by carbon shells that are incompletely graphitized. The encapsulation of the  $GdC_2$  crystal within the graphitic carbon shell may occur via one or a combination of two modes. The completion of the crystallization of the carbon polyhedral shell may occur from the outside in, causing a reduction in the volume of the carbon surrounding the  $GdC_2$  crystal. Such a phenomenon would account for the presence of a void adjacent to the carbide crystal inside the graphitic shell. More likely, the placement of the 12 pentagons to close the polyhedral shell and the polyhedron structure is simply incompatible with the shape of the engaged  $GdC_2$  crystal, causing the formation of a void. Figure 6 illustrates a high-resolution image of a completely crystallized carbon polyhedron containing a single crystal of  $\alpha$ - $GdC_2$  and a void region.

Although the concentration of Gd-filled nanoparticles was high, filled nanotubes themselves were observed only on extremely rare occasions. An example of such a metal-filled nanotube is shown in Fig. 7.

As is evident from Fig. 7, the end of the

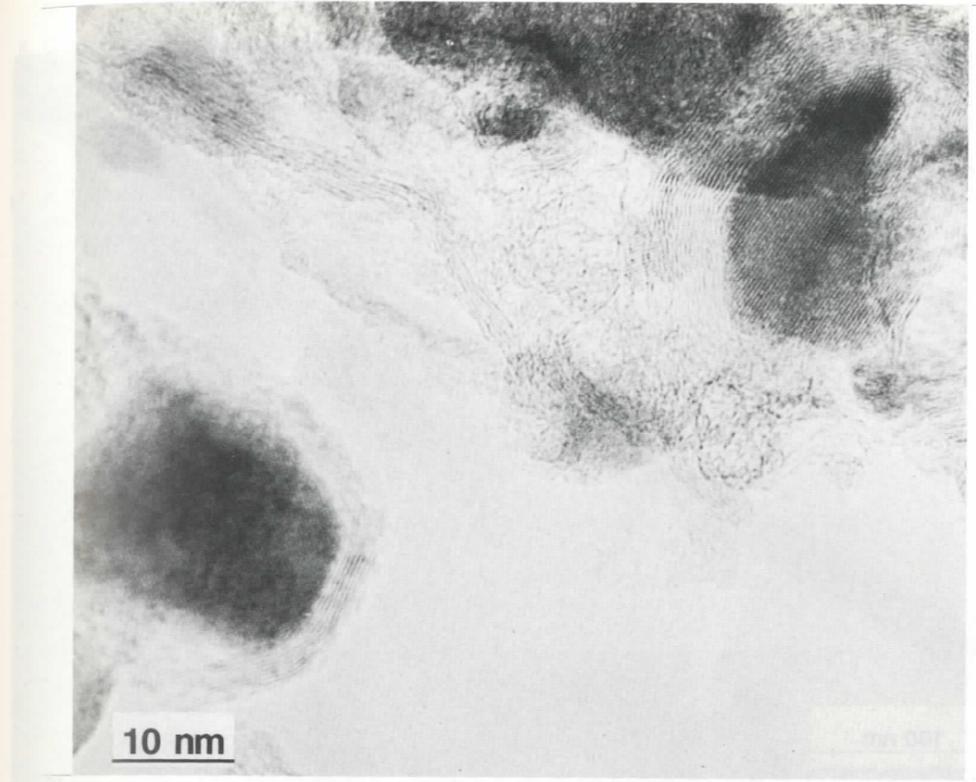


Fig. 5. High-resolution TEM image showing partial encapsulation of carbide crystals by graphitic layer planes.

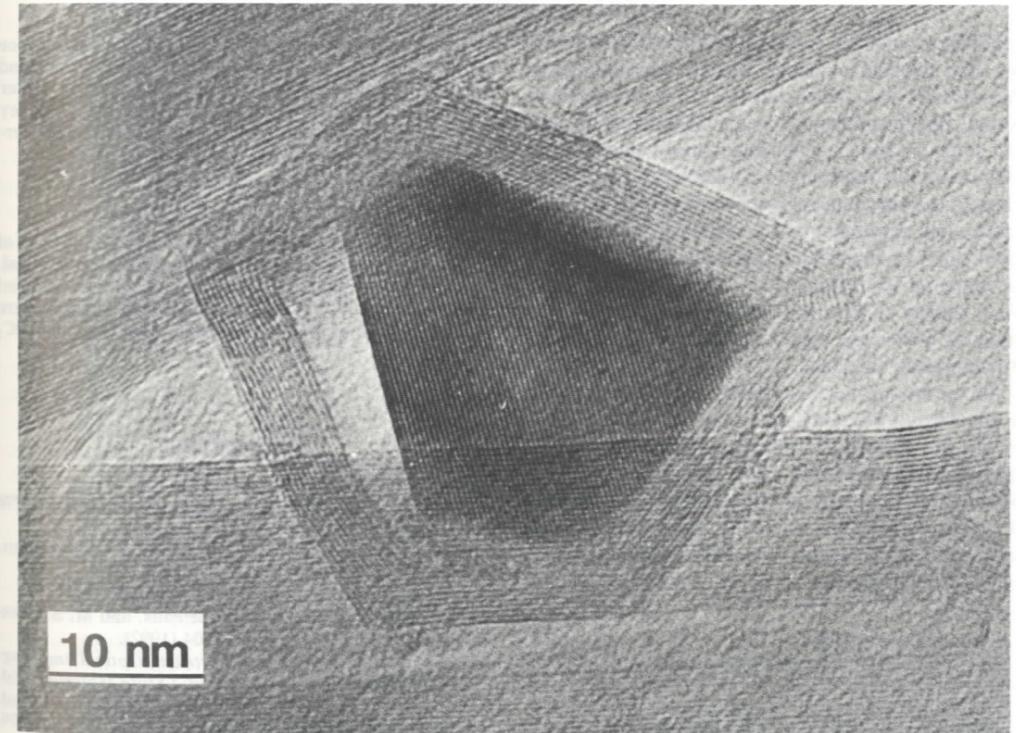


Fig. 6. High-resolution TEM image of a completely crystallized carbon polyhedral shell containing a single crystal of  $\alpha$ - $GdC_2$  and a void region. The particle is lying adjacent to several carbon nanotubes.

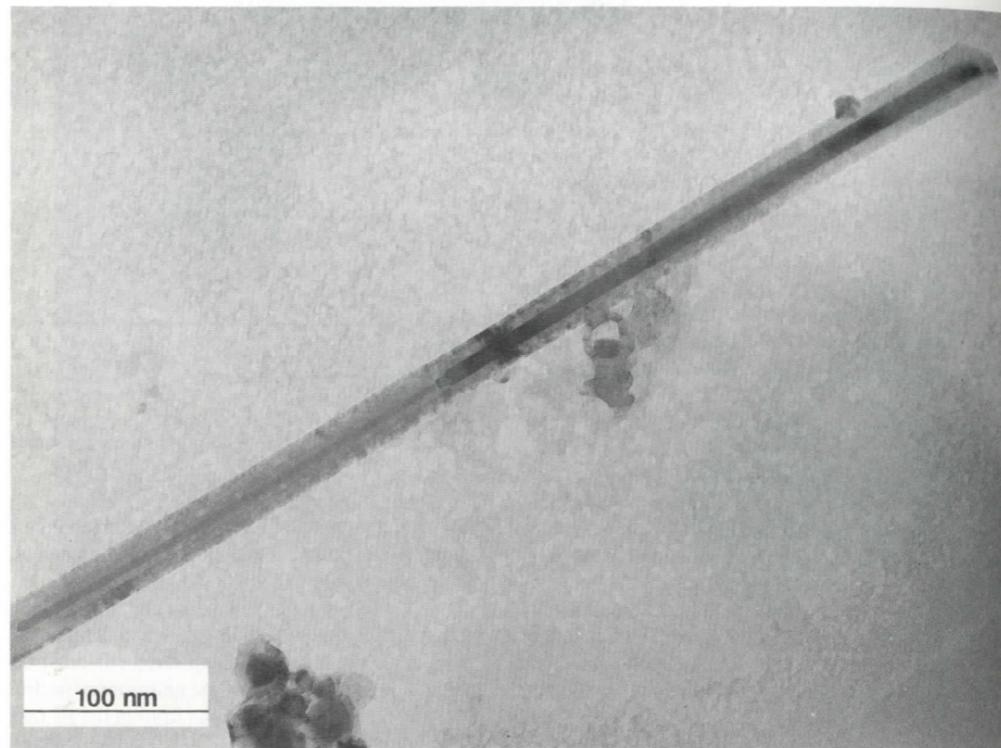


Fig. 7. Bright-field TEM micrograph of metal-filled carbon nanotube. It appears unlikely that the Gd material was drawn in by capillary action.

multilayer nanotube is capped by many carbon layers. It is therefore unlikely that the Gd material in the interior was drawn into the tube by capillary action. Furthermore, the meniscus indicates a contact angle greater than  $90^\circ$  (measured value is about  $135^\circ$ ), which is indicative of non-wetting behavior. Thus, if the Gd material were drawn in by capillary action, one would have to involve the unlikely scenario that this material expands upon solidification to cause an inversion of the meniscus. Since we were unable to observe lattice fringes in the Gd material inside the tube, we could not assign its stoichiometry or phase.

In summary, we have been able to encapsulate single crystals of  $\alpha$ -GdC<sub>2</sub> in carbon polyhedral shells by DC arc-discharge techniques. However, unlike encapsulated polyhedra of  $\alpha$ -LaC<sub>2</sub>, encapsulated GdC<sub>2</sub> is paramagnetic, and can be easily extracted at room temperature. Useful applications of such nanometer sized particles can be expected in several fields of technology.

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Project administered by the Agency of Industrial Science and Technology, the Ministry of International Trade and Industry, Japan. We thank the staff of the National Center for Electron Microscopy (NECM), Lawrence Berkeley Laboratory for assistance with TEM measurements performed there.

*Note added in proof:* Another study of encapsulates of gadolinium carbide has recently appeared, Majetich *et al.* *Phys Rev B* 48, 16845 (1993); these authors have studied encapsulated Gd<sub>2</sub>C<sub>3</sub>, in contrast to the work reported here by us, which is of the more strongly paramagnetic GdC<sub>2</sub> encapsulates.

#### REFERENCES

1. S. Iijima, *Nature* **354**, 56 (1991).
2. S. Iijima, T. Ichihashi, and Y. Ando, *Nature* **356**, 776 (1992).
3. J. W. Mintmire, B. I. Dunlap, and C. T. White, *Phys. Rev. Lett.* **68**, 632 (1992).
4. N. Hamada *et al.*, *Phys. Rev. Lett.* **68**, 1579.
5. R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, *Phys. Rev. B* **46**, 1804 (1992).
6. J. W. Mintmire *et al.*, In *Electrical, Optical and Magnetic Properties of Organic Solid State Materials* (Edited by L. Y. Chiang, A. F. Garito, and D. J. Sandman), MRS Symposia Proceedings No. 247, p. 339. Materials Research Society, Pittsburgh, PA (1992).
7. K. Tanaka, K. Okahara, M. Okada, and T. Yamabe, *Chem. Phys. Lett.* **191**, 469 (1992).

8. G. Overney, W. Zhong, and D. Tomanek, *Z. Phys. D* **27**, 93 (1993).
9. J. R. Heath *et al.*, *J. Am. Chem. Soc.* **107**, 7779 (1985).
10. Y. Chai *et al.*, *J. Phys. Chem.* **95**, 7564 (1991).
11. R. D. Johnson *et al.*, *Nature* **355**, 239 (1991).
12. L. Moro, R. S. Ruoff, D. C. Lorents, R. Malhotra, and C. H. Becker, *J. Phys. Chem.*, **97**, 6801 (1993).
13. R. S. Ruoff, D. C. Lorents, B. Chan, R. Malhotra, and S. Subramoney, *Science* **259**, 346 (1993).
14. G. Adachi *et al.*, In *Handbook of the Physics and Chemistry of Rare Earths*, Vol. 15, p. 164. (Edited by K. A. Gschneidner, Jr. and L. Eyring). North-Holland (1991). In *Handbook of Chemistry and Physics* (Edited by D. R. Lide). CRC Press, Ann Arbor, MI (1992).
15. B. D. Cullity, *Elements of X-Ray Diffraction*, p. 502. Addison-Wesley, Reading, MA (1978).
16. R. Lallemand, U.S. Dept. Com., Clearinghouse Sci. Tech. Inform. AD 627224, **11** (1965).
17. F. F. Luborsky, *J. Appl. Phys.* **32**, 1918 (1961) and references therein.