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Preparation and properties of carbon-coated magnetic nanocrystallites

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Carbon-coated gadolinium carbide nanocrystallites are generated by a process based on the Kratschmer-Huffman carbon-arc method of preparing fullerenes, and a novel magnetic-field-gradient separation technique is used to separate them. This separation of nanocrystalline byproducts of the carbon arc process is a prerequisite for many of the proposed applications of these materials. While the data presented pertain to Gd_2C_3, this method is generally applicable to any paramagnetic or ferromagnetic compound. Structural characterization by x-ray and electron diffraction and high-resolution transmission electron microscopy reveal the presence of a single gadolinium-containing (Gd_2C_3) phase and excess carbon. The carbide phase exists as 10–50 nm spherical particles. SQUID magnetometry shows paramagnetic response attributed to Gd^{3+} ions.

Carbon-coated metal carbide nanocrystallites such as LaC_2 nanoparticles are an intriguing byproduct of endohedral fullerene production.[1,2] Here we describe the preparation of similar magnetic nanocrystallites, along with a novel method for separating them. The data discussed are for paramagnetic gadolinium carbide, but we have also produced and separated paramagnetic holmium and ferromagnetic iron, cobalt, nickel, and manganese bismuth by this method. Results concerning these materials are discussed elsewhere.[3–5] The magnetism of these materials enables them to be isolated from nonmagnetic byproducts, unlike in the case of LaC_2.

The modified carbon-arc method efficiently synthesizes magnetic nanoparticles by a totally different process than those used to make γ-Fe_2O_3 nanocrystallites.[6,7] The ferromagnetic metal or metal carbide nanocrystallites are of interest for potential applications in which iron oxide particles are currently used: in magnetic data storage, for magnetic toner in xerography, in ferrofluids, and as contrast agents in magnetic resonance imaging. This carbon coating may also be useful in preventing corrosion in rare-earth permanent magnets.

In addition to a description of the process for producing and separating carbon-coated metal carbide nanoparticles, we present measurements on the structure and magnetic properties of gadolinium carbide.[8] In the process $\frac{1}{4}$ inch diameter graphite rods were drilled and packed with a mixture of metal oxide powder (in this case Gd_2O_3) and a combination of graphite powder and graphite cement, then heat treated and used in the upper electrode position in an ac carbon arc.[9] We used a 1:1 volume ratio of Gd_2O_3 and graphite powder bound together with a minimal amount of graphite cement. The rods were baked overnight at 300 °C to drive off water vapor. The arc conditions were 100 A and 25 V, along with a helium gas pressure of 125 Torr.

The isolated soot included a mixture of graphitic particles, carbon-coated magnetic nanocrystallites (here gadolinium carbide), and various fullerenes. Until now chemical methods have been used exclusively to separate the different fullerene components from each other. Here we targeted gadolinium because it has a large effective magnetic moment, $7.94\mu_B$, enabling magnetic as well as chemical separation techniques. This procedure extracts either ferromagnetic or paramagnetic particles. Similar methods have been used to extract magnetic components from coal and from various clays, but to our knowledge this approach has not been applied to the fullerenes. Application of this approach to the separation of magnetic endohedral fullerenes is discussed elsewhere.[10]

The raw soot was magnetically separated by first grinding it to a fine, micron-sized powder with a mortar and pestle, and then passing it through a magnetic-field gradient to separate magnetic from nonmagnetic species. The separator consisted of a funnel, an electrically grounded aluminum tube with a pair of $1\times1\times1/2$ in. neodymium iron boron permanent magnets ($M_r = 1.3$ T, Crucible Materials Corporation) on either side, and a pair of collection flasks. The grounded metal tube was necessary to prevent electrostatic charging of the powder. A paramagnetic particle experiences a gravitational force plus a magnetic force proportional to the field gradient, the field $\mathbf{H}$, and the susceptibility χ:

$$\mathbf{F}_M = \chi(\mathbf{H}\cdot\nabla)\mathbf{H} . \quad (1)$$

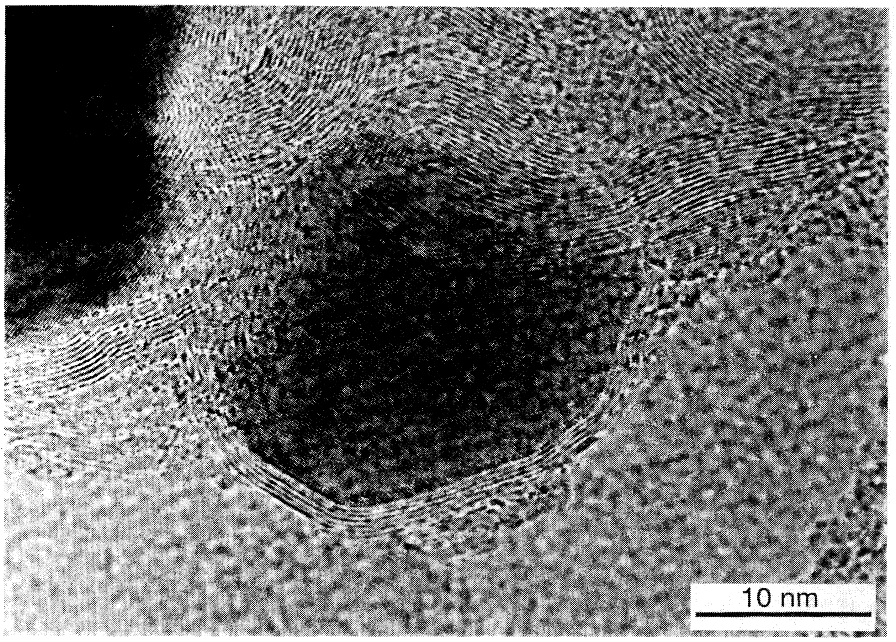

FIG. 1. Transmission electron micrograph of a gadolinium carbide nanocrystallite enclosed by several curved graphitic sheets, taken with a JEOL 4000 high resolution TEM.

The tube was positioned between the magnets to maximize $\mathbf{F}_M$. When small amounts of powder were poured through the apparatus, the magnetic species were suspended, while a nonmagnetic fraction passed through. The collection bottles were switched, and the tube was moved away from the magnets to release the magnetic powder. After the first pass, roughly one-eighth of the original volume was found to be magnetic. This powder was ground again and passed through repeatedly to enhance the abundance of magnetic material. This magnetic "filtrate" contains a mixture of magnetic nanocrystallites discussed here, embedded in a glassy carbon matrix, along with some fullerenes. The fullerenes were separated by extraction in carbon disulfide.[11] No visible differences were observed between pure carbon soot and the gadolinium-containing mixture. However, when cobalt nanocrystallites were produced, the soot had a flakier appearance.

The structural properties of the magnetic powder were examined first by electron microscopy. Scanning electron microscopy (SEM) revealed submicron-sized spherical particles. Energy dispersive x-ray fluorescence spectroscopy indicated that the gadolinium was uniformly distributed in the sample. Closer inspection was made with a JEOL 4000 400 keV, high-resolution transmission electron microscope (HRTEM). Samples were prepared by dispersing the powder in methanol with the aid of ultrasound and drying a drop of the solution on an amorphous carbon-coated copper grid. Gadolinium carbide nanocrystallites encapsulated in curved graphitic shells (Fig. 1), along with smaller crystallites and fullerene-sized clusters enclosed in amorphous carbon were observed. Curved, layered graphite structures appeared throughout the sample, but nodules rather than tubes predominated. In some of the larger (~50 nm diameter) nanocrystallites up to fifty graphitic layers were seen. Some of the particles were faceted, and a characteristic angle of ~120° between adjacent facets was noted. Unlike observations for similarly produced $\mathrm{LaC_2}$ nanocrystallites[1,2] no voids were observed between the carbide and carbon phases.

X-ray diffraction (XRD) of the nanocrystallites with a Rigaku diffractometer revealed peaks indicating the presence of a single $\mathrm{Gd_2C_3}$ phase, along with the prominent graphitic peaks and a broadened peak at small angles characteristic of the fullerenes. Comparison with tabulated crystal structures[12] suggests that the most abundant phase other than graphite is the paramagnetic body-

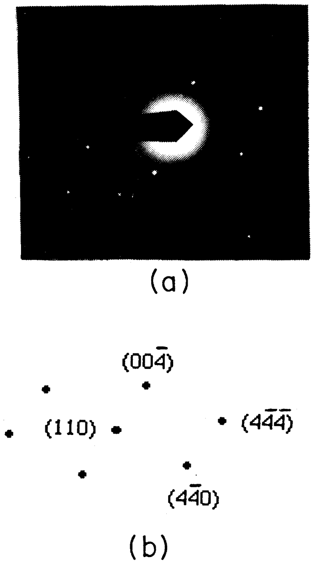

FIG. 2. (a) Electron diffraction pattern of a single $\mathrm{Gd_2C_3}$ nanocrystallite oriented on a [110] axis. (b) Enlarged diagram of (a) identifying several reflections. The electron diffraction pattern for bcc $\mathrm{Gd_2C_3}$ along a [110] axis was fit using Desktop Microscopist$^{\mathrm{TM}}$ software.

centered cubic Gd_2C_3. Our structural assignment is on the basis of x-ray diffraction peaks as well as electron diffraction. No evidence was seen for α-GdC_2, Gd_2C, or Gd_2O_3 phases, or for Gd crystallites in either XRD or TEM data. This observation of the sesquicarbide phase is significantly different from the case of lanthanum doping, where the more carbon-rich α-LaC_2 phase was observed.[1,2] We estimated our starting materials had an ~0.02 Gd/C molar ratio consistent with the La/C molar ratio of Ref. 1. Our observation of the more Gd-rich Gd_2C_3 phase would therefore not seem to be a result of compositional difference but may be indicative of different thermodynamic conditions.

Electron microscopy and x-ray diffraction results were compared for consistency. TEM showed regions containing small embedded clusters roughly the size of C_{60}, but we assume a mixture of fullerenes exist in the sample. Most of the magnetically separated soot contained gadolinium carbide nanocrystallites coated with roughly five to ten curved graphitic sheets. Electron diffraction of a typical crystallite oriented in the [110] direction corroborated the identification of body centered cubic Gd_2C_3 (Fig. 2). The presence of Gd_2C_3 has also been verified through electron microscopy.

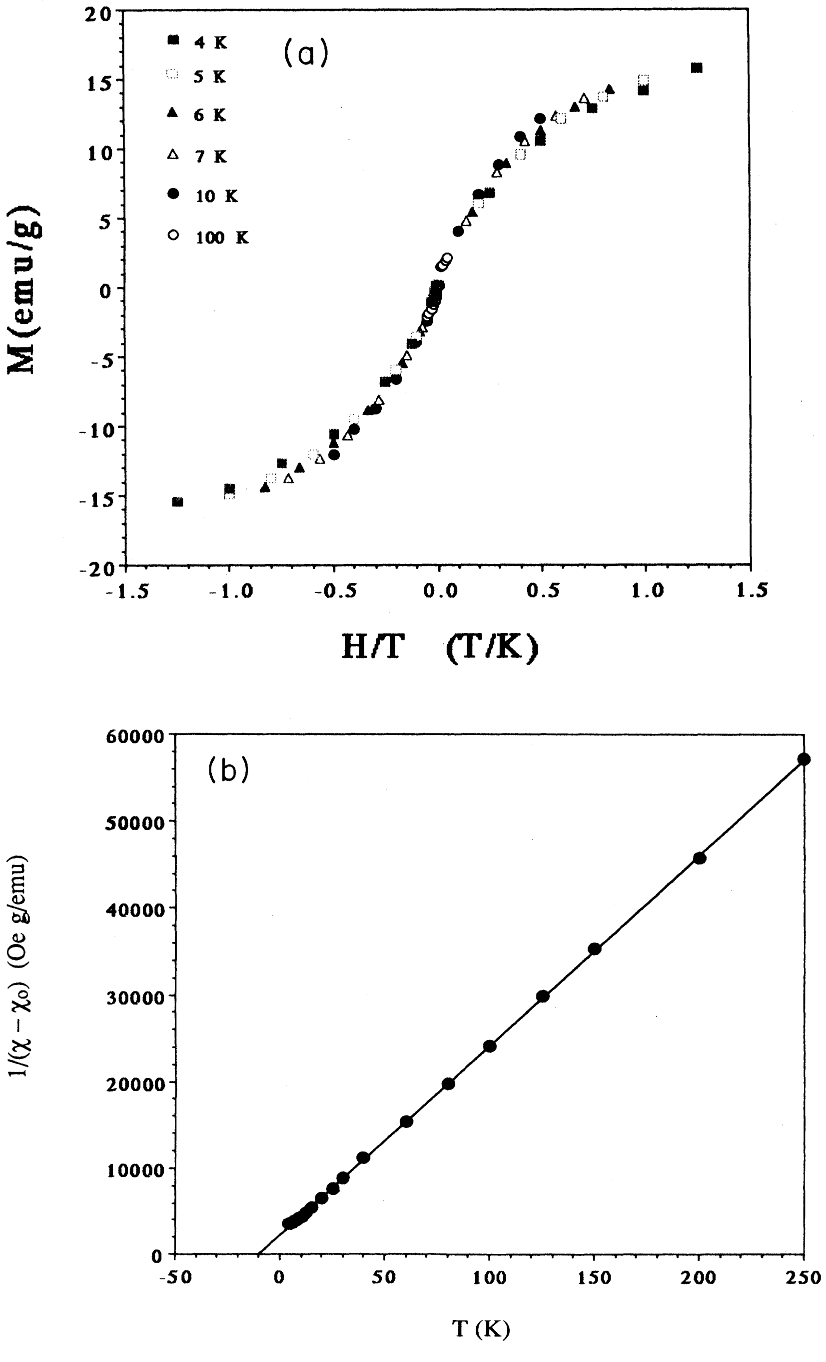

FIG. 3. (a) Magnetization (emu/g) vs H/T for data sets collected at 4, 5, 6, 7, 10, and 100 K exhibiting a characteristic paramagnetic scaling consistent with a Gd^{3+} ground state. (b) Curie-Weiss fit to inverse susceptibility vs temperature data taken in a 5 T fixed field.

Room-temperature electron paramagnetic resonance spectra of the powder at 9.104 GHz showed a single broad derivative centered at 3130 G, corresponding to a g value of 2.08. This is nearly consistent with the $g=2$ predicted for a $J=S=\frac{7}{2}$ ground state for a Gd^{3+} ion.

Magnetization data for powder samples, enriched in Gd_2C_3 nanocrystallites by magnetic separation, has been obtained employing a Quantum Design superconducting quantum interference device magnetometer. $M(H,T)$ has been determined in solenoidal fields between ±5 T and for temperatures from 4 to 300 K. Figure 3(a) shows scaled magnetization data as a function of H/T for data sets collected at 4, 5, 6, 7, 10, and 100 K. These data are seen to fall on a universal curve, indicating paramagnetic response. This universal curve is well fit by a $J=\frac{7}{2}$ Brillouin function,

$$B_J(x)=\frac{(2J+1)}{2J}\coth\frac{(2J+1)}{2J}-\frac{1}{2J}\coth\frac{x}{2J}\ , \tag{2}$$

where $x=gJ\mu_B H/k_B T$ and $g=2$. This is consistent with a Gd^{3+} ionic ground state as observed in several bulk GdC_x phases. Bulk gadolinium metal exhibits ferromagnetism, but the gadolinium carbide nanoparticles showed only paramagnetic response. The magnetic behavior of bulk gadolinium carbide is unknown. Figure 3(b) shows inverse magnetic susceptibility (corrected by χ_0) as a function of temperature for a fixed applied field of 5 T. This is also clearly consistent with a paramagnetic state. Fits to a Curie-Weiss law,

$$\chi-\chi_0=\frac{C}{(T+\theta)}\ , \tag{3}$$

using Mathematica™ software yield a Curie temperature of -10.42 K and a Curie constant, $C=4.56\times10^{-3}$ emu K/g Oe (per gram of sample). Now if $J=\frac{7}{2}$ and $g=2$ for Gd^{3+} ions as previously shown, then an effective magnetic moment per Gd^{3+} ion of $g[J(J+1)]^{1/2}\mu_B=7.94\mu_B$ is predicted, giving rise to a Curie constant of 5.01×10^{-2} emu K/g Oe (per g of Gd^{3+} ions). This result indicates that only ~9% of the sample (by weight) is Gd^{3+} ions, suggesting that the magnetic separation could be optimized by further breaking up agglomerated or embedded particles.

This encapsulation method, in combination with the magnetic separation technique, has been successfully applied to other magnetic species, in particular those containing holmium, cobalt, and iron. A similar Ho_2C_3 phase is formed while Co, which is not a strong carbide former, is observed as *ferromagnetic* carbon saturated fcc particles. Iron forms a ferromagnetic cementite phase. The nanocrystalline phases produced therefore appear to be specific to the metal used, but the production and separation processes are generally applicable to both paramagnetic and ferromagnetic species. The magnetic behavior of these other materials is more complicated and will be reported in more detail elsewhere.[3-5] In the case of Co and Fe_3C, the additional complexity takes the form of superparamagnetism. For Ho_2C_3 paramagnetic behavior is observed, but the low symmetry crystal field splits the Ho^{3+} ground state, leading to deviations from free ion paramagnetism, and from the magnetic behavior of bulk Ho_2C_3.

We have reported a method for separating magnetic nanocrystallites prepared by a carbon-arc method. This separability enables studies of fine-particle magnetism in a new class of compounds, some of which have significant technological potential.

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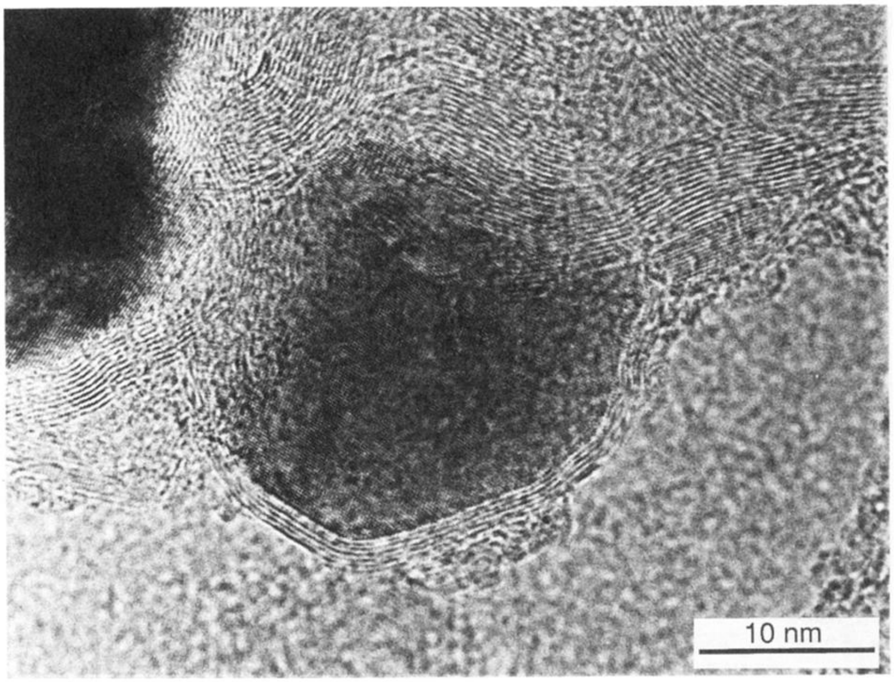

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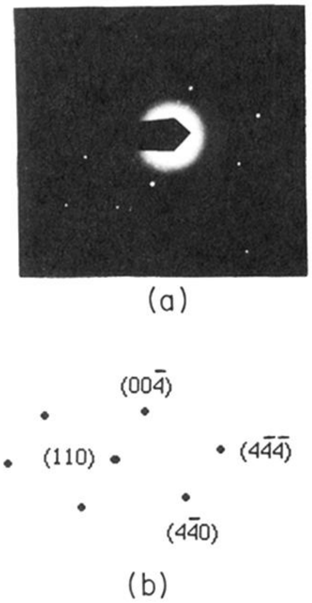

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