

Figure 4 shows the phase diagram of carbon according to Bundy<sup>7</sup>. Although diamond is the stable phase at room temperature and 2 GPa, it is not possible to produce it under normal conditions because of the extremely low kinetics of the process. Bulk diamond crystals can be made to grow from graphite only when the temperature is raised at least several hundred degrees above room temperature either under shock treatment ( $P > 30$  GPa,  $T > 1,100$  K)<sup>8</sup> or in the presence of a catalyst such as molten nickel ( $P > 6$  GPa,  $T > 1,200$  K)<sup>9</sup>. The difficulty comes from the high stability of the graphitic planes, which melt only above 4,000 K. The transformation from this planar  $sp^2$  structure to the diamond  $sp^3$  network is difficult, and extreme temperatures and pressures are necessary to induce the transformation. The role of the catalyst in the present industrial processes is, in part, to dissolve carbon from graphite, which then precipitates to form the allotrope stable at that temperature and pressure (diamond). Although  $C_{60}$  can be considered as a folded graphite sheet, we must take into account the fact that in the pentagons<sup>10</sup> the predominant hybridization is  $sp^3$ . This may make the transformation of  $C_{60}$  into diamond easier. A dense assembly of  $C_{60}$  spheruloids<sup>6</sup>, where 48 out of 60 carbon atoms have quasi-tetrahedral coordination, is sterically fairly close to that of diamond, implying that a small rearrangement of the atoms can result in the change of structure. The fact that we need nonhydrostatic conditions to trigger the reaction may be due to an instability of  $C_{60}$  molecules to uniaxial or shear stresses. Fullerenes are probably very stable to isotropic stress, resulting in homogeneous deformation<sup>1</sup>, but they possibly cannot resist being squeezed anisotropically. □

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## Electron paramagnetic resonance studies of lanthanum-containing $C_{82}$

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THE conjecture that atoms can be trapped inside closed carbon cages such as the fullerenes was first made by Kroto *et al.*<sup>1</sup>. Mass spectroscopic evidence obtained soon after<sup>2</sup> suggested that lanthanum atoms were encapsulated in fullerenes prepared by laser vaporization of a lanthanum-impregnated graphite disk, and these results were later corroborated<sup>3,4</sup>. Recently, helium atoms have been incorporated into fullerenes through collisions in the gas phase<sup>5</sup>, and evidence has been obtained for the formation of metal-containing fullerenes during arc burning of composite graphite rods<sup>6</sup>. All of these studies, however, have produced quantities too small for characterization using standard spectroscopic techniques. We report here the preparation of milligram quantities of lanthanum-containing  $C_{82}$ , which can be solvent-extracted in yields of about 2% along with empty  $C_{60}$  and  $C_{70}$  cages. We have

measured the electron paramagnetic resonance spectrum of this mixture, both in solution and in the solid state, which reveals that the lanthanum atom has a formal charge of 3+, and the  $C_{82}$  a charge of 3-. This runs contrary to some expectations that the doubly charged fulleride anions would be the most stable species<sup>6,7</sup>; it also reveals that the fullerene cages have the same formal charge as in the superconducting alkali-metal-doped phases<sup>8,9</sup>.

Our samples were prepared by using a composite rod made of graphite and  $La_2O_3$ . The materials were mixed with a binder (dextrin), partially dried and pressed into a rod. After annealing at 150 °C, the rod was heated to 1,400 °C for 2 h. The soot produced by arc vaporization of the rod under helium at 200 Torr was extracted with toluene, and the extract was washed with diethyl ether and dried. The resulting powder was analysed using mass spectrometry and electron paramagnetic resonance (EPR) spectroscopy.

The time-of-flight mass spectrum of material laser-desorbed from the dry powder (Fig. 1) shows large peaks for  $C_{60}$ ,  $C_{70}$  and  $La@C_{82}$ . The inset in Fig. 1 shows the fragmentation pattern found for  $La@C_{82}$  when the intensity of the ionization laser (wavelength 193 nm) was increased. This pattern is consistent with the pairwise removal of carbons from the skeletal cage, with the La atom remaining inside the resulting smaller fullerene<sup>3</sup>. The two groups of peaks centred about 15 mass units above the  $C_{60}$  and  $C_{70}$  peaks are due to 25% <sup>13</sup>C-enriched  $C_{60}$  and  $C_{70}$  left over in the arc chamber from an earlier burn and inadvertently vacuumed up along with the material produced for this experiment.

The X-band (9.112 GHz) EPR spectrum of the degassed dry powder shown in Fig. 2a is centred at  $g = 2.001$ , with a hint of rich structure and an overall width of ~10 gauss. No other EPR peaks were detected for 2,500 gauss either side of the field corresponding to  $g = 2$ . The intensity of the EPR signal shows that the  $La@C_{82}$  accounts for  $2 \pm 1\%$  (by weight) of the sample, close to the 3.5% estimated from X-ray photoelectron spectroscopy on the same material. The powder was then dissolved in 1,1,2,2-tetrachloroethane, degassed several times using a freeze-thaw cycle and sealed in a 5-mm thin-walled pyrex tube. The solution EPR spectrum, shown in Fig. 2b, consists of eight extremely narrow (0.125 gauss) equally spaced (1.25-gauss interval) lines of equal intensity also centred at  $g = 2.0010$ , with additional intensity in between. The measured  $g$  value is similar to those found for fullerene anion radicals<sup>10–13</sup>, which range from 1.995 to 2.001. The main eight-line spectrum is unambiguously diagnostic for isotropic hyperfine coupling to a nuclear magnetic moment with spin 7/2 (ref. 14), the value for the <sup>139</sup>La nucleus, showing that the unpaired electron has spin

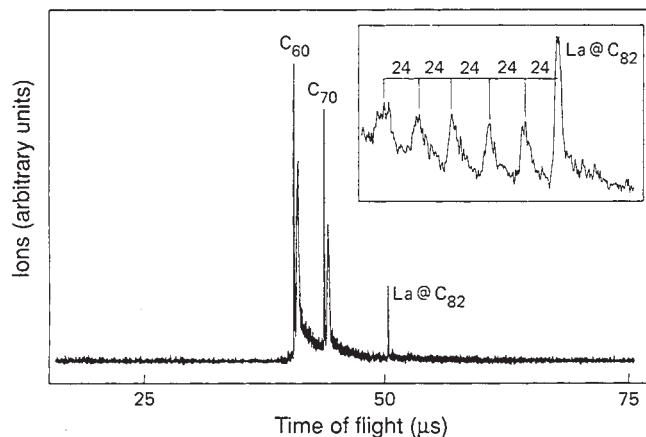


FIG. 1. Mass spectrum of material laser-desorbed from the toluene extract (dried) resulting from arc burning of a composite rod of graphite and  $La_2O_3$  (see text). The inset shows how the peak due to  $La@C_{82}$  loses carbons two at a time under strong laser irradiation. The abscissa in the inset is time but the progressive change in mass from peak to peak is shown explicitly.

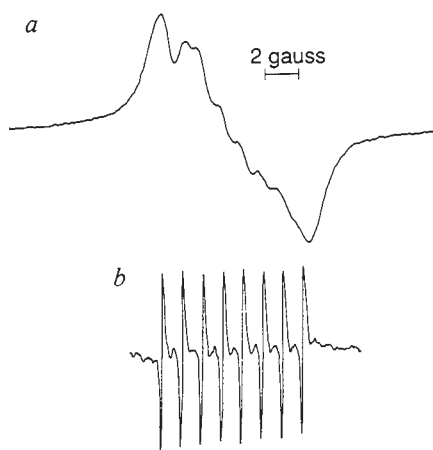


FIG. 2 EPR spectrum (9.112 GHz) at ambient temperature of (a) solid degassed toluene extract (dried) resulting from arc burning of a composite graphite/La<sub>2</sub>O<sub>3</sub> rod and (b) a degassed solution of the dried extract in 1,1,2,2-tetrachloroethane.

density on the lanthanum atom. But the <sup>139</sup>La hyperfine coupling constant (1.25 gauss) is very small; in contrast, the coupling measured<sup>15</sup> for a La<sup>2+</sup> defect generated in a CaF<sub>2</sub> lattice (the only experimental value we could find in the literature) is ~50 gauss at 20 K. Furthermore, a calculation of the hyperfine coupling for La<sup>2+</sup> was made using spin-polarized unrestricted Hartree-Fock wavefunctions and yields a value of 186 gauss. Therefore the small value of the observed hyperfine coupling constant indicates that the lanthanum atom is in the 3+ oxidation state. This is consistent with calculations of the electronic structure of La@C<sub>60</sub>, which found a 3+ charge for the lanthanum atom in that species<sup>16</sup>. Figure 2b shows that there are intensity maxima between all the La lines. As 60% of the La@C<sub>82</sub> moieties will contain at least one <sup>13</sup>C, this intensity is consistent with hyperfine coupling to <sup>13</sup>C in natural abundance; the spectrum is expected to be broadened because of the large number of inequivalent carbons in the C<sub>82</sub> cage<sup>7</sup>. A key point, however, is that observation of coupled electron, <sup>139</sup>La and <sup>13</sup>C spins provides direct evidence for the association of a La atom with the C<sub>82</sub> framework.

The EPR spectra reveal a *g* value consistent with a fullerene anion radical and a La atom in the 3+ oxidation state. We are thus led to a picture of the electronic structure of La@C<sub>82</sub> in which the La 6s electrons pair in the lowest unoccupied molecular orbital of C<sub>82</sub> while the third electron occupies the next higher energy orbital. Although this leaves La in a diamagnetic oxidation state, polarization of the atomic orbitals by the paramagnetic  $\pi$ -electron system of C<sub>82</sub><sup>3-</sup> results in unpaired spin density at the site of the <sup>139</sup>La nucleus. Therefore, we believe that La<sup>3+</sup>@C<sub>82</sub><sup>3-</sup> is a ground-state doublet, rather than a closed-shell species as proposed previously<sup>6,7</sup>, and furthermore that the paramagnetism originates in an unpaired electron spin in the  $\pi$ -electron system of the carbon framework.

An interesting aspect of this result is that the captive ion (La<sup>3+</sup> in this case) is relatively unperturbed because the interaction with the cage electrons is small. Thus, we have in this bulk sample a large number of single isolated ions at high concentration (~2% of the molecules), potentially making many spectroscopic studies possible. Efforts to separate the empty fullerenes from metal-containing C<sub>82</sub> by chromatography are currently in progress. □

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## Long-lived photoinduced charge separation in a redox system trapped in a sol-gel glass

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A KEY feature in the mechanism of photosynthesis is the initial storage of a substantial fraction of the light energy in the form of a long-lived radical pair<sup>1</sup>. In attempts to mimic this process in artificial systems<sup>2–4</sup>, impressive progress has been made in increasing the efficiency of the charge-separation reaction between an excited photosensitizer and an appropriate electron acceptor, but prevention of the energy-wasting back-reaction to neutral species still constitutes a major challenge. The back-reaction limits the length of time during which charge separation (and thus energy storage) can be maintained. Here we report exceedingly long-lived (up to a few hours) photoinduced charge separation in an artificial photosynthetic system that does not require a secondary substrate to react with the charged species. Our system uses pyrene (Py\*) as the photosensitized electron donor and *N,N'*-dimethyl-4,4'-bipyridinium (methyl viologen, MV<sup>2+</sup>) as the electron acceptor, both immobilized in a porous sol-gel silica glass<sup>5</sup>. The redox reaction is carried out by the mediation of a third mobile charge carrier in the intrapore space<sup>6</sup>. The spatial separation between the donor and acceptor inhibits the back-reaction to produce the long lifetimes of the charge-separated pair.

Energy storage in artificial photochemical systems generally involves the reaction between an excited photosensitizer A\* and an appropriate electron acceptor B:



The back-reaction (2), which in homogeneous solutions is usually diffusion-controlled, must be slowed down to allow the radical pair formed in reaction (1) to undergo subsequent (catalytic) processes leading to useful energy-rich products. Long-lived charge separation is generally achieved by carefully designing heterogeneous environments for carrying out the reaction<sup>2,3</sup>. Radical pairs with lifetimes of minutes have been produced in such systems<sup>7–11</sup>. For example, Moser *et al.*<sup>11</sup> observed a relatively high yield of long-lived charge carriers in an Fe(III)-doped TiO<sub>2</sub> colloidal semiconductor<sup>4</sup>.

The photochemical reaction system used here involves the reduction of immobilized *N,N'*-dimethyl-4,4'-bipyridinium chloride (methyl viologen, MV<sup>2+</sup>) to MV<sup>•+</sup> by immobilized excited-state pyrene (Py\*), through mediation by the mobile charge carrier, *N,N'*-tetramethylene-2,2'-bipyridinium bromide

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