Evidence for high-temperature ferromagnetism in photolyzed C_{60}

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C_{60} transforms to a polymeric phase where the C_{60} molecules are bonded to form a chain structure when it is subjected to ultraviolet radiation at ambient temperature in the absence of oxygen. The electron paramagnetic resonance spectrum of C_{60} photolyzed in the presence of a low pressure of oxygen or in air shows a very broad, asymmetric derivative signal at room temperature and at a magnetic field position well removed from $g=2.000$. With decreasing temperature, the broad line shifts to lower magnetic fields and increases further in linewidth, as expected for a ferromagnetic resonance signal. A low-field nonresonant derivative signal is also observed, consistent with the existence of ferromagnetism. Ferromagnetism up to room temperature in photolyzed C_{60} is confirmed unequivocally by superconducting quantum interference device measurements of the dc magnetization as a function of magnetic field. A possible model for the origin of ferromagnetism based on these results and Raman data on photolyzed samples is also proposed.

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Photoinduced magnetism is of considerable interest in data storage applications because of its potential to perform reading as well as writing of information. The phenomenon has been widely investigated in several different materials over the past decade, but has been observed mostly in metal-based compounds and at relatively low temperatures. Here we report evidence for photogenerated ferromagnetism at room temperature and above in polymeric C_{60}, produced in the presence of oxygen, which confirms earlier largely overlooked investigations.[1,2] In the earlier studies Murakami and Suematsu[1] and Makarova *et al.*[2] provide magnetic data and suggest that room-temperature magnetism occurs in an oxygenated polymeric C_{60} generated by ultraviolet irradiation. In subsequent work, Makarova and co-workers[3] report ferromagnetism up to 500 K in a high-pressure polymerized C_{60} rhombohedral phase, where it is suggested that ferromagnetism arises due to the presence of defect patterns. Ferromagnetism has also previously been observed in TDAE-C_{60}, tetrakis(dimethylamino)ethylene-fullerene[60], below 16 K.[4,5] In this paper we present ferromagnetic resonance and low-field data coupled with superconducting quantum interference device (SQUID) dc magnetometery results to support the existence of ferromagnetism above 300 K in a photopolymerized C_{60} phase. A structural model of the ferromagnetic phase is also suggested.

99.9%-pure polycrystalline C_{60} obtained from Aldrich contained in evacuated quartz tubes was subjected to 254 nm ultraviolet radiation for 4 h. The vacuum was typically 10^{-2} Torr, which meant that the sample was still exposed to a small level of oxygen. It has been shown in previous work that irradiation for 21 h in high vacuum does not produce the ferromagnetic phase.[1] In agreement with this we find that the ferromagnetic phase cannot be produced when the sample is irradiated in flowing helium. Irradiation in flowing oxygen forms the phase. The results described below could also be obtained by ultraviolet irradiation of polycrystalline C_{60} for 20 h in air at ambient temperature. Both the vacuum and air-irradiated samples were examined by Raman spectroscopy using a JobinYvon-Horiba LabRam microRaman spectrometer using approximately 2 mW of 632.8 nm laser radiation at the sample. A shoulder at 1458 cm^{-1} downshifted in frequency by about 10 cm^{-1} from the pentagonal pinch mode frequency at 1469 cm^{-1} of pristine C_{60} had been produced by ultraviolet irradiation. The appearance of this line is clearly indicative of the transformation of part of the sample to a linearly polymerized C_{60} phase via a $2+2$ cycloaddition reaction.[6,7] The polymeric phase in the photolyized sample has been shown to be an oligomer having typically less than 20 C_{60} units.[6]

The irradiated samples were then transferred to a quartz tube which had not been previously subjected to ultraviolet light and magnetic resonance spectra recorded in a Varian E9 electron paramagnetic resonance spectrometer operating at 9.2 GHz. Figures 1(a) and 1(b) show the spectra obtained at 300 and 104 K for the sample irradiated in air. The narrow derivative signal observed is due to the small fraction of C_{60} anions in pristine C_{60}.[8] These paramagnetic species are likely to be the origin of the paramagnetism observed at low temperatures in the SQUID magnetization data discussed below. Only the narrow derivative signal is observed in the pristine C_{60} used in this study. The very broad, asymmetric line has not previously been observed in irradiated C_{60}. The resonance has the characteristics of a ferromagnetic resonance (FMR) signal, as discussed below, indicating that the sample is ferromagnetic. The line markedly broadens as the temperature is lowered from room temperature and the mag-

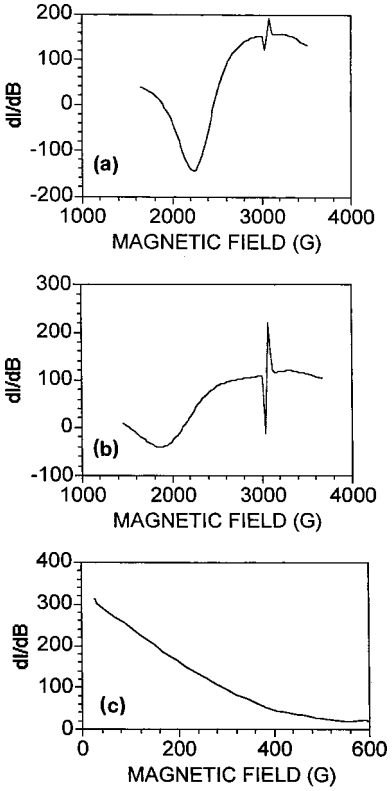

FIG. 1. (a) Ferromagnetic resonance spectrum (derivative of the absorption intensity I with respect to the magnetic field B) observed in ultraviolet irradiated C_{60} at (a) 300 K and (b) 104 K, showing a marked increase in width and shift of the broad line to lower magnetic field values with decreasing temperature. (c) Low-field nonresonant spectrum (derivative of the absorption intensity I with respect to the magnetic field B) measured at 300 K in ultraviolet-irradiated C_{60}.

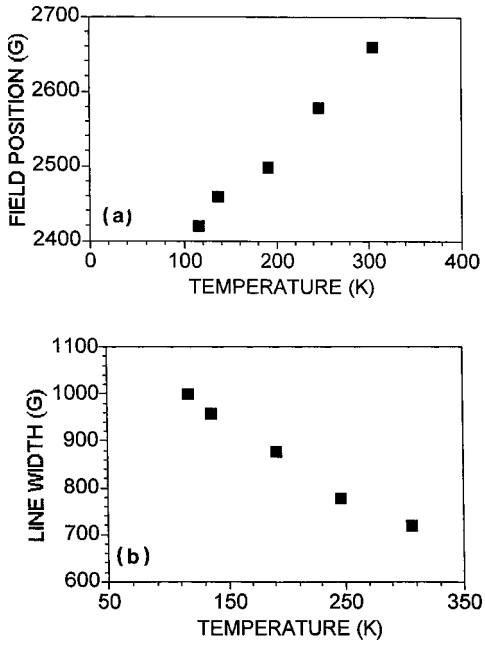

FIG. 2. (a) Temperature dependence of the magnetic field at the center of the ferromagnetic resonance for irradiated C_{60}. (b) Temperature dependence of the linewidth of the ferromagnetic resonance for photopolymerized C_{60}.

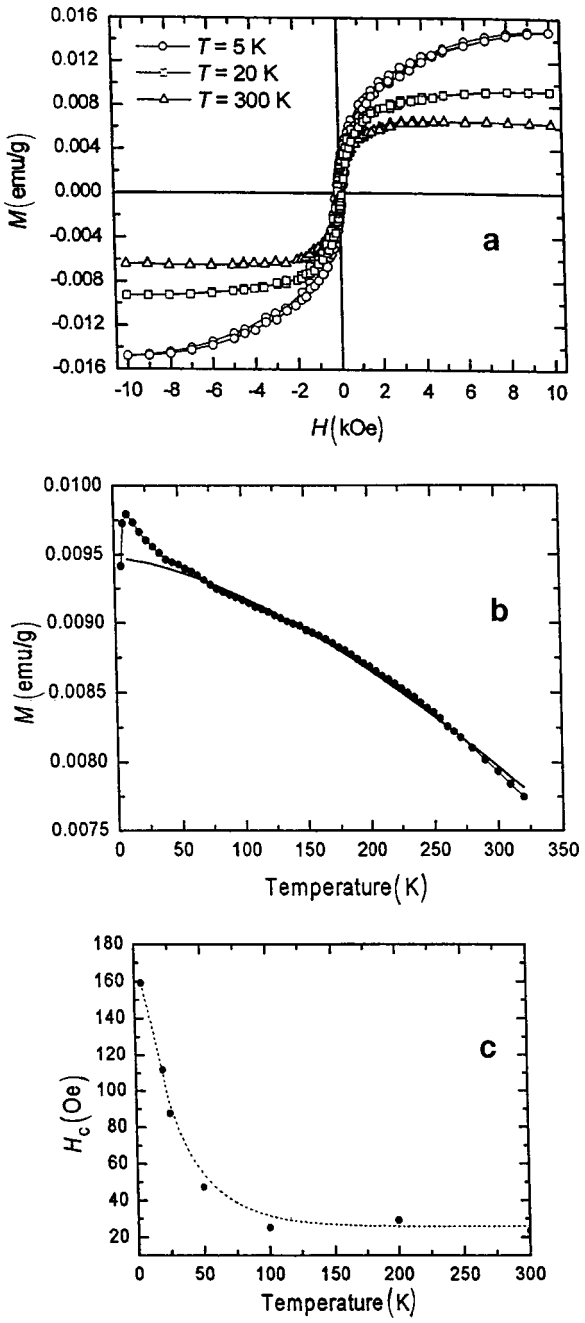

FIG. 3. (a) Magnetization as a function of dc magnetic field at 5, 20, and 300 K measured using a SQUID magnetometer. Paramagnetic (PC) and diamagnetic (DC) contributions have been subtracted out. (b) Temperature dependence of the magnetization. The line through the data is a fit to the Bloch law. (c) Temperature dependence of the coercivity.

netic field position of the line shifts to lower dc magnetic fields. Figures 2(a) and 2(b) show the dependence of the magnetic field shift of the center of the line and linewidth, respectively, as a function of temperature. This behavior is clearly not typical of electron paramagnetic resonance (EPR) spectra of free radicals, but is characteristic of spectra observed for ferromagnetic solids arising from ferromagnetic resonance.[9] Generally, EPR signals of radicals show slight line narrowing and small shifts in the field dependence of the

resonance as the temperature is lowered. On the other hand, the field position of ferromagnetic signals is usually quite temperature dependent because of the dependence of the resonant field position on the magnetization and anisotropy constant. The specific functional dependence depends on the geometric shape of the sample.[9] A similar broadening and shift to lower magnetic fields is observed for the resonance spectrum of C_{60}-TDAE in its ferromagnetic phase below 16 K.[10] Heating the sample to 460 K did not decrease the intensity of the FMR signal, indicating that the ferromagnetic phase is stable at least up to 450 K.

Further evidence for ferromagnetism is the observation of a low-field, nonresonant derivative signal using EPR [Fig. 1(c)]. This low-field microwave absorption signal is a well-established signature for the existence of ferromagnetism. It arises because the permeability in a ferromagnetic solid depends nonlinearly on the strength of the applied dc magnetic field at low fields.[11,12] Since the surface resistance is proportional to the square root of the permeability, the microwave absorption at low field is detected as the derivative of the nonresonant absorption as a function of the applied dc magnetic field.

Further support for the existence of ferromagnetism in irradiated C_{60} was obtained by SQUID magnetometry using a Quantum Design MPMS2 magnetometer. Magnetic hysteresis loops at 5, 20, and 300 K shown in Fig. 3(a) clearly indicate the presence of ferromagnetism in a fraction of the solid. SQUID magnetometry on the starting sample of pristine C_{60} showed only weak paramagnetism at low temperature and a diamagnetic component, both of which were subtracted out of the data shown in Fig. 3(a). The diamagnetic component is independent of temperature, having the value -0.00365 emu/g in a 300-Oe magnetic field. The paramagnetic component is temperature dependent, having a classic Curie-Weiss $(1/T)$ temperature dependence. At 300 K in a 300-Oe magnetic field it has the value 5.53×10^{-5} emu/g. Figure 3(b) gives the temperature dependence of the magnetization. The line through the data is a fit to the Bloch law:

$$M(T)=M_s(0)[1-AT^{3/2}] \tag{1}$$

for $A=3.1\times10^{-5}$ emu/g $K^{3/2}$ and $M_s(0)=9.5$ memu/g. In principle, T_c can be estimated from this fit of the data to the temperature at which $M(T)$ is zero, which gives a T_c of 1000 K, but deviations from the Bloch law near T_c due, for example, to critical fluctuations make this an overestimate. It is estimated from the relative intensities of the Raman bands of C_{60} and oligomers that 20% of the sample is polymerized, giving a corrected saturation magnetization at room temperature of 0.04 emu/g. Figure 3(c) gives the temperature dependence of the coercivity (H_c). Normally at T_c, H_c will be zero; however, because of the weak dependence on temperature above 150 K, it is not possible to estimate T_c from the data.

In any report of ferromagnetism in an organic material the purity of the sample is a critical issue and we have paid considerable attention to sample analysis. The starting C_{60} solid was analyzed by induction coil plasma mass spectrometry (ICP-MS). The results indicated that signals from all metals were at levels well below 100 parts per 10^9. Plasma-induced atomic absorption spectroscopy independently confirmed iron levels to be less than a few parts per 10^9. Further, the EPR of the C_{60} before photolysis, which would readily detect magnetic metals at parts per 10×10^9 did not show any evidence for magnetic metals.

A number of photoelectron emission studies have shown that C_{60} molecules undergo polymerization and oxidation when subjected to uv irradiation in the presence of oxygen or air.[13,14] The process involves an initial photolytic dissociation of molecular oxygen to atomic oxygen, which then bonds to C_{60}. The oxygenated C_{60} then forms the dimers and oligomers. Since the ferromagnetic phase is not produced when the irradiation occurs in high vacuum, Murakami and Suematsu suggested that oxygenated C_{60} dimers or oligomers are the source of the ferromagnetism.[1] However, it is also necessary to account for the source of the unpaired electron required to form the ferromagnetic phase. It is known that the C_{60} anion is more stable than C_{60} and gives rise to an EPR signal in pristine C_{60}.[8] A possibility is that some of the anions are incorporated in the oligomers, providing the necessary unpaired electron. In fact, it has been shown that charged monomers have a lower barrier toward the formation of C_{60} dimers compared to neutral dimers.[15]

In conclusion, FMR data in combination with SQUID measurements provide evidence for the existence of ferromagnetism in C_{60} photolyzed in air. We expect that the fraction of the magnetic phase can be increased by the photolysis of thin-film samples. Thin-film samples would also allow study of whether light could be used to remove the ferromagnetic state. This would raise the possibility of using polymerized C_{60} films deposited on flexible, low-cost plastics as a light-activated room-temperature magnet with both reading and writing capabilities.

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