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Magnetism of carbon clusters

R. C. Haddon
AT&T Bell Laboratories, Murray Hill, New Jersey 07974-0636

Alfredo Pasquarello
Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA) PHB-Ecublens, CH-1015 Lausanne, Switzerland

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The π-electron ring current magnetic susceptibilities and endohedral chemical shifts of the fullerenes are calculated with the London theory. The diamagnetism calculated for the fullerenes that have been characterized to date does not show a monotonic increase toward the graphite value. By carrying out calculations on high-symmetry giant fullerenes (C_n) in the size regime $100 < n < 1000$, we are able to demonstrate the beginnings of such a trend. In particular C_{540} is calculated to exhibit more than 10% of the π-electron ring current magnetic susceptibility of graphite on a per carbon basis. Endohedral chemical shifts are predicted to be invariant to cluster size, but subject to the quantum size effects seen in smaller fullerenes and metallic clusters. The fullerenes are different from the metallic clusters because the finite band gap in conjugated carbon compounds allows the diamagnetic term to dominate at large cluster size. The experimentally observed decrease in nanotube material diamagnetism with temperature is attributed to the increased importance of the Van Vleck term due to finite-temperature effects.

The magnetism of the fullerenes has been of interest since the original report of the observation of these species.[1] The large diamagnetism of graphite suggests that the fullerenes might also display strong π-electron ring currents and an enhanced magnetic susceptibility. Furthermore if C_{60} is viewed as a sphere with 60 free electrons which can respond to the application of a magnetic field, then the ring current diamagnetism is expected to be 41 times that of benzene.[2] However, calculations using the London theory predicted a vanishingly small π-electron ring current magnetic susceptibility due to the cancellation of the diamagnetism by a very strong Van Vleck paramagnetic term.[2,3] Experimental measurements of the magnetic susceptibility soon after the bulk synthesis of the fullerenes confirmed the basic findings of the London calculations.[4,5]

More recently, measurements of the ^{3}He nuclear magnetic-resonance chemical shifts of the endohedral fullerenes He@C_{60} and He@C_{70} have provided further information on the magnetism of the two lowest fullerenes.[6] The interpretation of the chemical shifts of the ^{3}He nuclei in terms of π-electron ring currents is somewhat uncertain due to the magnetic shielding contribution which arises from the localized σ electrons. However, the experimental shifts of $\delta = -6$ ppm (^{3}He@C_{60}) and -29 ppm (^{3}He@C_{70}) with respect to free ^{3}He are in at least qualitative agreement with the results from the London theory[2,7] and in good agreement with detailed Hartree-Fock (HF) calculations of the total endohedral shielding.[8,9]

A number of authors have interpreted the increase in diamagnetism of C_{70} over C_{60} in terms of the expected trend in fullerene magnetism toward that of graphite.[4-6] Nevertheless, London calculations on two isomers of C_{84} did not reflect such a progression,[10] showing π-electron ring current magnetic susceptibilities much smaller than that of C_{70} (although subsequent work has shown that the C_{84} isomers considered in this study do not correspond to those isolated from the bulk fullerene synthesis). Furthermore HF calculations find a smaller shielding in ^{3}He@C_{76} than ^{3}He@C_{70}.[8] It therefore seemed at least possible that the higher curved forms of carbon (clusters consisting of giant fullerenes, onions and nanotubes), might not approach the very large diamagnetism known to be characteristic of graphite. Recent work on bulk samples of material obtained from the nanotube synthetic method (which is known to give such an inhomogeneous distribution of carbon clusters), has now provided evidence for an extremely strong diamagnetism in this form of carbon.[11] In particular the carbon cluster samples show a diamagnetism slightly greater than that of highly oriented pyrolytic graphite (HOPG) at room temperature, which increases in magnitude at low temperatures eventually exceeding the HOPG value by a factor of 2.5.

In the present work we employ the finite field version of the London theory to examine the π-electron ring current contribution to the diamagnetic susceptibility of the known lower fullerenes and some of the high-symmetry giant fullerenes. We find that for fullerenes (C_n), with n less than about 100, the magnetic susceptibility fluctuates with size in an apparently random manner. We attribute this to quantum size effects of the type seen by van Ruitenbeek and van Leeuwen (RL),[12] in their model calculations of small metallic systems. In high-symmetry fullerenes, however, we demonstrate the beginnings of a trend toward the very large diamagnetism now known to be operative in large carbon clusters and graphite. The present results differ from those obtained on metallic systems in that the large bandwidth and molecular nature of these conjugated carbon compounds ensures

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that there is a substantial band gap and this places them in the low-temperature regime where diamagnetism still dominates at large size. The experimentally observed decrease in diamagnetism as the carbon cluster samples are brought to room temperature is explained in terms of the breakdown of this approximation and the increased contribution of Van Vleck paramagnetism due to finite-temperature effects.

We use the finite field version of the London theory as originally described by Elser and Haddon. Full discussions of this method are already available.[2,3,7] Briefly, London modified the resonance or transfer integrals (β_{ij}) between pairs of conjugated carbon by a field-dependent phase factor. The tight-binding Hamiltonian is given by

$$H_{ij}=\beta_{ij}\exp(i\theta_{ij}) \tag{1}$$

with the applied magnetic field (H) along z

$$\theta_{ij}=\frac{1}{2}(x_i y_j - x_j y_i)\frac{e}{\hbar}cH \; . \tag{2}$$

For small values of the field, the π-electron ring current magnetic susceptibility (χ_{RC} or χ_{π}^{2}) is obtained directly from the energy (E)

$$-\frac{1}{2}\chi_{\mathrm{RC}}H^2=E(H)-E(0) \; . \tag{3}$$

The chemical shifts due to the π-electron ring currents (δ_{RC}), are obtained by including a probe dipole in the vector potential.[2,3,7]

We follow previous practice and quote the ring current magnetic susceptibilities in units of the value for benzene with the magnetic-field perpendicular to the plane of the ring. Various empirical estimates have been provided for this quantity but our previous value of χ_{RC} (benzene-perp) $= -34\pm7$ ppm emu/mol ($\beta=2.66$ eV),[4] covers most of the literature estimates and is utilized in the present work. The analyses of Haberditzl[13] and Dauben, Wilson, and Laity[14] surveyed a wide range of conjugated hydrocarbons and they obtained a value of -41.1 ppm emu/mol, which is utilized for the comparison with graphite. The rotationally averaged value[15] for the π-electron ring current contribution[16] to the magnetic susceptibility is χ_{RC} (graphite) $= -83$ ppm emu/C $\simeq 2\times\chi_{\mathrm{RC}}$ (benzene-perp). Note that to make a direct comparison between the π-electron ring current magnetic susceptibilities of graphite and benzene, χ_{RC} (graphite) must be multiplied by a factor of 3 to allow for the anisotropy of the graphite value, and by a further factor of 6 to normalize the benzene value to a per carbon basis. From this standpoint the π-electron ring current contribution to the magnetic susceptibility in graphite is 36 times that of benzene. For the chemical shifts we use the same parametrization as that adopted for the magnetic susceptibilities. Error estimates are not available for the chemical shifts, but for the reasons discussed below they are expected to be at least as large as those incurred in the magnetic susceptibilities.

The experimental detection of ring currents by magnetic-susceptibility measurements or NMR chemical shifts is made difficult by the presence of localized contributions to the magnetic susceptibility of organic molecules. In the case of C_{60} the localized contributions constitute most of the observed magnetic susceptibility and in a molecule as unusual as C_{60} the appropriate correction is rather uncertain. For the local contribution to the magnetic susceptibility of network conjugated carbon atoms the following values (sources) have been considered: $\chi_{\mathrm{local}}(\text{C-net})=-4.85$ ppm emu/C (hydrocarbons),[13,14] -4.37 (hydrocarbons),[17] -3.70 (strained hydrocarbon),[17] -4.8 (graphite).[15] For the fullerenes, we use the previously adopted value[4] of -4.37 ± 0.67 ppm emu/C. It is likely that a larger diamagnetic contribution is appropriate for the less curved clusters.

Buhl *et al.*[9] have calculated that relative to free ^{3}He the chemical shifts of the saturated endohedral compounds are $^3\mathrm{He@C_{60}H_{60}}$ $\delta=-5.2$ ppm and $^3\mathrm{He@C_{70}H_{70}}$ $\delta=-5.4$ ppm. Thus the ring currents are not solely responsible for the observed ^{3}He chemical shifts in the en-

TABLE I. Calculated magnetic properties of C_{60} and C_{70}.

			Theory[a]		
Property	Compd.	Local	π-electron ring current	Total	Expt.
χ (ppm emu/mol)	C_{60}	-262 ± 40	17 ± 4	-245 ± 44	-260 ± 20[4]
			-68 ± 14	-330 ± 54	-250[5]
	C_{70}	-305 ± 50	-241 ± 50	-546 ± 100	-550 ± 50[4]
			-197 ± 40	-502 ± 90	-500 ± 40[5]
δ (ppm)	C_{60}	-5.2	1.2	-4.0	-6.3[6]
			-4.9	-10.1	
	C_{70}	-5.4	-13.9	-19.3	-28.8[6]
			-11.4	-16.8	

[a] For each molecule the first line of theory entries is calculated with the resonance integrals of all bonds set equal to the benzene value (β). The second line of entries is calculated with resonance integrals ($k\beta$) scaled for bond length (l) with reference to the benzene value (β): $k=\exp(\Delta l/0.3727)$, with $\Delta l=l_B-l$ and l_B the benzene bond length (1.397 Å); see L. Salem, *Molecular Orbital Theory of Conjugated Systems* (Benjamin, New York, 1966). See text for parametrization.

dohedral fullerenes and the anisotropic shielding of the localized σ electrons must be considered. We use these values[9] directly; in the general case a localized shielding contribution of $\delta_{\text{local}}(^3\text{He@C}_n) = -5.5 \pm 2$ ppm would probably be appropriate. The results for the two experimentally characterized fullerenes, C_{60} and C_{70}, are shown in Table I. The magnetic susceptibilities are well described by the calculations. The best results seem to be obtained by setting all resonance integrals to a common value (first line of entries in Table I) rather than by scaling with the bond strength. The empirical analyses used in the parametrization also used this simplification.[13,14] The chemical shifts are not as well described as the magnetic susceptibilities, particularly in the case of C_{70}, but are expected to be adequate to account for the trends. We have previously discussed the calculation of fullerene chemical shifts[7]—the principal problem seems to originate with the use of line currents to represent the electron flow in fullerenes. Because of the asymmetry between the electron-density distribution inside and outside the fullerene surface,[18] this problem is more severe than in conventional planar conjugated hydrocarbons, where such an approximation works rather well. This problem should become less significant with increasing fullerene size, where the details of the current flow become less important in estimating the secondary magnetic field at the center of the fullerene.

The calculated π-electron ring current magnetic properties for all of the fullerene isomers which have been structurally characterized to date are included in Table II (C_{60} is listed in Table III). The molecular geometries are taken from the modified neglect of differential overlap (MNDO) calculations of Raghavachari.[19] Of the neutral fullerenes, C_{70} shows the largest ring current magnetic susceptibility, and based on this set of molecules no clear trend is discernible. In fact there are no obvious depen-

TABLE II. Calculated π-electron ring current magnetic properties of anisotropic fullerenes.

Compd charge	χ_{RC} (rel benzene)[a]				δ_{RC} (ppm)[a]			
	x	y	z	av	x	y	z	av
$C_{70}(D_{5h})$	6.49	6.49	4.36	5.78	−12.9	−12.9	−8.4	−11.4
−2	2.04	2.04	3.88	2.65	−3.9	−3.9	−8.4	−5.4
−6	2.87	2.87	4.69	3.48	−5.2	−5.2	−9.4	−6.6
−12	3.80	3.80	6.04	4.55	−6.9	−6.9	−13.5	−9.1
$C_{76}(D_2)$	2.95	5.21	5.42	4.53	−5.6	−9.4	−8.9	−8.0
−2	8.53	0.40	3.21	4.05	−15.9	−0.9	−6.1	−7.6
−4	−269	4.50	7.47	−86	511.9	−8.2	−12.3	163.8
−6	5.96	8.68	13.77	9.47	−11.2	−15.1	−21.9	−16.0
−12	−1.52	1.90	−0.38	0.00	3.3	−3.0	0.6	0.3
$C_{78}(C_{2v},1)$	6.68	3.20	1.40	3.76	−11.9	−5.4	−1.8	−6.4
−2	−1.99	2.74	5.77	2.17	3.0	−4.7	−9.2	−3.6
−4	5.58	9.60	9.92	8.37	−9.6	−16.0	−15.8	−13.8
−6	5.04	6.46	13.27	8.26	−8.6	−10.5	−20.9	−13.3
−12	7.72	−1.58	−2.74	1.14	−13.4	2.7	4.4	−2.1
$C_{78}(C_{2v},2)$	4.71	4.87	3.82	4.47	−8.7	−8.4	−5.6	−7.6
−2	3.26	7.76	7.75	6.26	−5.8	−12.7	−12.5	−10.4
−4	5.58	2.29	14.62	7.50	−10.2	−3.6	−22.7	−12.2
−6	3.30	−0.46	1.03	1.29	−5.5	1.2	−1.4	−1.9
−12	1.98	0.36	−1.85	0.17	−3.5	−0.6	2.9	−0.4
$C_{78}(D_3)$	5.03	5.03	−0.01	3.35	−8.4	−8.4	0.2	−5.6
−2	4.26	4.26	10.88	6.47	−7.6	−7.6	−19.8	−11.7
−6	14.95	14.95	4.56	11.49	−23.8	−23.8	−8.5	−18.7
−12	−2.24	−2.24	−5.71	−3.40	3.9	3.9	11.6	6.5
$C_{82}(C_2)$	3.32	3.42	3.43	3.39	−5.3	−5.4	−5.1	−5.3
−2	8.45	6.17	8.77	7.80	−13.7	−9.9	−12.8	−12.1
−4	−0.16	7.20	12.90	6.65	0.1	−11.3	−18.6	−9.9
−6	6.29	10.75	12.65	9.90	−10.3	−16.6	−18.6	−15.1
−12	−2.66	−1.94	−4.65	−3.08	5.2	3.4	6.9	5.2
$C_{84}(D_{2d})$	1.21	3.48	3.48	2.72	−1.5	−5.3	−5.3	−4.0
−4	10.95	9.17	9.17	9.76	−16.1	−13.4	−13.4	−14.3
−6	17.51	9.04	9.04	11.86	−25.9	−13.3	−13.3	−17.5
−12	−4.95	−1.29	−1.29	−2.51	7.3	2.0	2.0	3.8
$C_{84}(D_2)$	2.39	3.81	3.33	3.18	−3.6	−5.8	−4.7	−4.7
−2	−4.06	11.87	6.81	4.87	5.8	−17.4	−9.5	−7.1
−4	5.31	7.52	12.28	8.37	−8.2	−11.3	−17.5	−12.3
−6	13.85	9.17	11.83	11.62	−21.0	−13.6	−17.1	−17.2
−12	−1.67	−1.63	−4.42	−2.57	2.8	2.6	6.4	3.9

[a] Calculated with resonance integrals ($k\beta$) scaled for bond length, see footnote to Table I.

TABLE III. Calculated π-electron ring current magnetic properties of isotropic fullerenes.

Compd charge	χ_{RC} (rel benzene) $[\beta]$[a]	χ_{RC} (rel benzene) $[k\beta]$[b]	δ_{RC} (ppm) $[\beta]$[a]	δ_{RC} (ppm) $[k\beta]$[b]
$C_{60}(I_h)$	-0.5	2.0	1.2	-4.9
-6	14.8	12.9	-36.2	-31.5
-12	1.0	-2.1	-2.4	5.1
$C_{120}(T_d)$	11.2	11.3	-9.9	-9.9
-6	31.4	25.6	-28.0	-22.9
-12	6.9	0.7	-5.8	-0.3
$C_{180}(I_h)$	20.8	20.7	-9.9	-9.7
-6	60.5	51.9	-28.7	-24.6
-12	20.5	11.7	-9.7	-5.5
$C_{240}(I_h)$	35.3	34.1	-10.9	-10.4
-6	90.9	79.4	-28.0	-24.4
-12	34.6	19.0	-10.7	-5.9
$C_{540}(I_h)$	144.6	125.6	-13.3	-11.5
-6	264.4	224.8	-24.5	-20.8
-12	144.1	101.2	-13.3	-9.3

[a] Calculated with the resonance integrals of all bonds set equal to the benzene value (β).

[b] Calculated with resonance integrals ($k\beta$) scaled for bond strength, see footnote to Table I.

dencies in the results. Most of the fullerenes show the large diamagnetism in the -6 state and the small diamagnetism in the -12 that is characteristic of C_{60}, but even here there are obvious exceptions. Some of the fullerenes show very large anisotropies and it would be of interest to experimentally test these predictions. As with the previous study on C_{84} isomers, those that have been isolated and are included in Table II, are among those fullerenes with the smallest π-electron magnetic susceptibilities. We therefore sought to test whether the small susceptibilities would continue for the intermediate to large carbon clusters, that is, the giant fullerenes[20] (C_n), with $100 < n < 1000$.

We therefore extended our study to include C_{120}, C_{180}, C_{240}, and C_{540}—the structures of which were calculated by Bakowies and Thiel[21] in tetrahedral or icosahedral symmetry with the MNDO method. This choice of fullerene structures is clearly appropriate for examining the evolution of the fullerenes into nanotubes and eventually graphite because of their high symmetry, but may be less appropriate for the higher fullerenes which so far have shown a preference for low-symmetry structures.[19]

The high-symmetry fullerenes show clear trends (Table III). The behavior in the three oxidation states are parallel, and the magnetic susceptibilities now increase monotonically with fullerene size. This last statement is also true when the fullerene magnetic susceptibility is treated on a per carbon basis (Fig. 1). In the case of C_{540} the π-electron magnetic susceptibility is more than 10% of that of graphite on a per carbon basis. If the approximately linear dependence is continued, the symmetrical fullerenes would achieve parity with graphite at about C_{5000}.

Interestingly the chemical shifts remain approximately constant. If we use the graphite unit cell to approximate the surface area of the general fullerene (C_n), with bond length l, it may be shown that the radius (r) is given by[22]

$$r=(3^{3/4}/4\pi^{1/2})ln^{1/2} . \tag{4}$$

Using the relationship for spherical fullerenes[2]

$$\delta_{RC}=2\chi_{RC}/r^3 . \tag{5}$$

We obtain

$$\delta_{RC}=\frac{\chi_{RC}}{n^{3/2}}(128\pi^{3/2}/3^{9/4})l . \tag{6}$$

Given the approximately linear dependence of χ_{RC} on the fullerene size, n, the small variation of δ_{RC} is to be expected. Thus the endohedral chemical shift will be a sensitive analytical tool for the small fullerenes[6] but of less use in the regime of giant fullerenes, although the ability of the internal atom to move away from the center of the fullerene may lead to interesting effects.

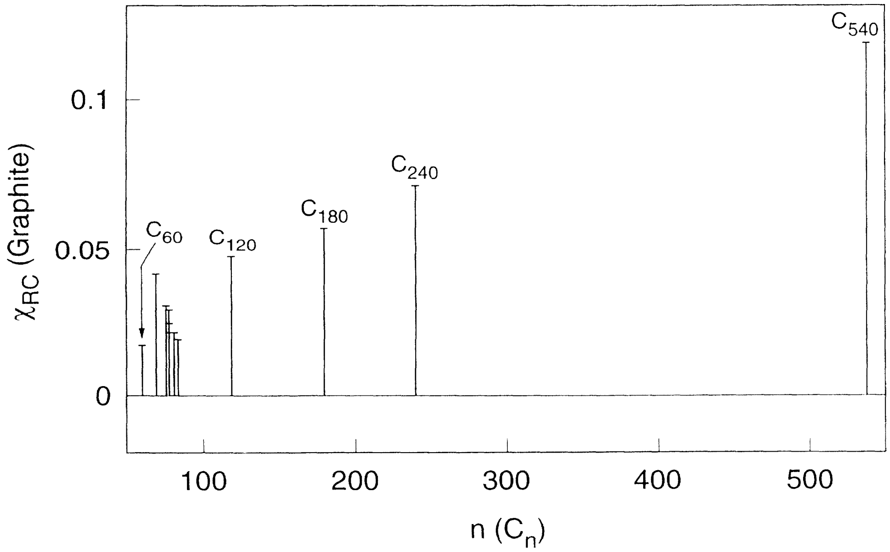

FIG. 1. π-electron ring current magnetic susceptibilities (χ_{RC}), as a function of fullerene size, $n(C_n)$, calculated with resonance integrals adjusted for bond strength ($k\beta$), see footnote to Table I.

Most of the other experimental and theoretical investigations of size-dependent magnetism in clusters have focused on systems for which the bulk form is metallic and the enhancement is paramagnetic.[12,23–27] The conjugated carbon clusters are unique in this respect in that graphite is a semimetal and in its two-dimensional form has a vanishingly small density of states at the Fermi level.[28] This apparently accounts for the differences between the carbon clusters and the metallic clusters. The energy gap, together with the large bandwidth which is characteristic of conjugated carbon compounds ensures that the cluster magnetism is usually dominated by the diamagnetic term. The experimentally observed decrease in nanotube diamagnetism at room temperature[11] is then attributed to the increased contribution of the Van Vleck term due to finite-temperature effects [although the division of the susceptibility between diamagnetic and paramagnetic (Van Vleck) terms is gauge dependent and therefore has no real physical significance]. Although the decrease in diamagnetism could arise from the population of excited states with nonzero spin, the small electron-spin-resonance signal[11] suggests that this effect does not make a large contribution to the magnetism of the nanotubes. The apparently random variations in fullerene magnetism in the size regime $n \sim < 100$, results from quantum-size effects, similar to those documented in model calculations by RL.[12]

In summary, we have used London calculations on known fullerenes and model giant fullerenes to provide a rationale for the magnetism of these species and the manner in which the magnetism approaches that of nanotube material and graphite. The carbon spheroids are different from other cluster compounds because the finite energy gap allows the diamagnetic term to dominate at large cluster size.

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