

provides an excellent control on the study. The theory for the solid solution is straightforward. Since the solid and liquid solvents have similar properties, it is expected and found that the transfer parameters are virtually the same in the two types of systems. The parameters obtained from the liquid data are, therefore, not arbitrary fitting parameters. The results demonstrate that, at least for this system, we have a clear description of the influence of spatial diffusion on photoinduced electron transfer.

In a subsequent study,²² results like those presented above will be combined with experimental measurements of the dynamics

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of electron back-transfer (geminate recombination) and theory. This will provide a description of the competition between back-transfer and radical ion separation by diffusion.

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Confirmation of a Vanishingly Small Ring-Current Magnetic Susceptibility of Icosahedral C₆₀

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In 1987, Elser and Haddon predicted a vanishingly small π -electron contribution to the magnetic susceptibility of the icosahedral C₆₀ molecule (buckminsterfullerene). This result runs counter to intuition and was subsequently disputed on the basis of ab initio computations. Following the recent discovery of methods for preparing (and purifying) large quantities of C₆₀, we here report measurements of the magnetic susceptibility, χ , of a solid sample of pure C₆₀ by SQUID magnetometry. The obtained mass value, $\chi_g = -0.35 \times 10^{-6}$, is far below that of graphite or benzene, consistent with the Elser-Haddon picture of accidental cancellation of the diamagnetic and paramagnetic contributions to χ . An estimate of the unusually large paramagnetic contribution is in accord with recent measurements of C₆₀'s electronic excitations. The C₇₀ molecule is also measured to have $\chi_g = -(0.59 \pm 0.05) \times 10^{-6}$.

Introduction

The recent discovery⁷ of a method for producing (and purifying^{8,9}) significant quantities of molecular allotropes of carbon, particularly the celebrated C₆₀ molecule (buckminsterfullerene), has made possible the measurement of material properties.¹⁰ One such property is the bulk magnetic susceptibility, χ , treated previously theoretically.^{1,4-6} The high symmetry (I_h) of the unique

structure proposed² and now confirmed^{7,10} for C₆₀, i.e., a hollow spherical bonding network resembling the laces of a football, implies that the susceptibility tensor is determined from a single measurement of χ .

Two theoretical approaches present strongly contrasting pictures of C₆₀'s magnetic properties.^{1,4-6} Kroto et al. first suggested² that icosahedral C₆₀ should exhibit strong magnetic shielding from π -electron ring-current effects (and by implication a large, negative χ); this quantity has immediate relevance to the NMR chemical shift of an atom trapped at the center of the icosahedral cage.¹¹ To examine this possibility, Elser and Haddon¹ (EH) calculated the magnetic properties of C₆₀'s π -electrons using the London method modified to treat Hückel molecular orbitals in three dimensions. They reported that "the magnetic response of C₆₀ is unlike that of any molecule yet encountered": Namely, there occurs an unusual cancellation of diamagnetic and paramagnetic contributions, so that the susceptibility is very small and has a sign that is sensitive to equilibrium geometry parameters (relative bond lengths).^{1,3} Subsequently, Fowler et al.⁴ (FLZ) used Hartree-Fock supercomputer calculations to conclude that C₆₀ should have a large, negative (diamagnetic) χ , analogous to that

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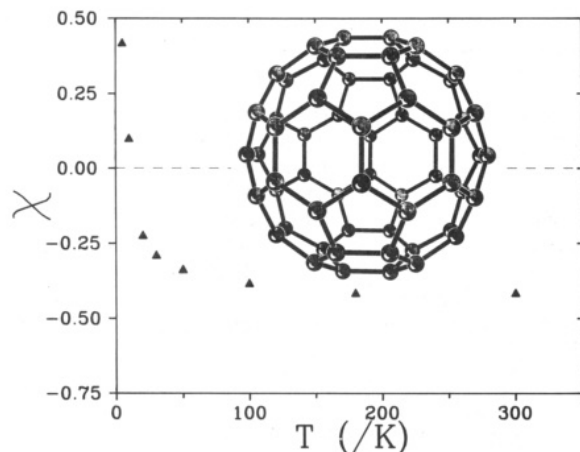


Figure 1. Measured magnetic susceptibility of a 0.066-g sample of C_{60} as a function of temperature. [The units are 10^{-6} emu.] After subtracting the contribution from the capsule, one finds a high-temperature value $\chi_g = -0.35 \times 10^{-6}$ in cgs units.

of benzene. However, the FLZ result was reanalyzed by Haddon and Elser⁵ as consistent with the EH result, after a local contribution is removed. Most recently, Schmalz⁶ took exception to this reanalysis and supported the contention that C_{60} responds as a normal aromatic molecule. It thus seems that there is an inconclusive theoretical debate regarding the experimental quantity that we have now measured.

Experimental Method

Samples of C_{60} and C_{70} are prepared as described previously.^{9,12} Evaporation of graphite under helium atmosphere followed by toluene extraction afforded a 30–40% yield of soluble carbon molecules, C_n . A half-gram quantity of the soluble extract is chromatographically separated on alumina into pure fractions— C_{60} , C_{70} , C_{76}/C_{78} , C_{84} , and higher ($n > 88$) using toluene–hexane (1:20 to 1:1 eluant). After solvent evaporation and drying, the infrared spectrum of the powdered C_{60} sample was recorded to check on residual hydrocarbon and revealed negligible toluene contamination. Magnetic measurements are made using a “SHE” SQUID magnetometer (Bio-Tech, Inc.). This instrument has a useful sensitivity of 10^{-6} emu in fields to 4.5 T and over the temperature range 5–300 K. A few measurements were repeated using a second magnetometer (Quantum Design, Inc.). Samples of C_{60} (0.066 g) or C_{70} (0.029 g) were enclosed in a gelatin capsule on a thread, for which a correction must be made.

Results

The magnetic susceptibility of the C_{60} sample is shown as a function of temperature (χ_g vs T) in Figure 1. This curve shows that at temperatures greater than 180 K the susceptibility is temperature-independent with a mass value of $\chi_g = -0.35 \times 10^{-6}$ (cm^3/g). A measurement on crushed graphite, following identical procedures, gave a result near the literature value. The same measurement performed on the C_{70} sample gave a somewhat larger value, $\chi_g = -(0.59 \pm 0.05) \times 10^{-6}$, where the uncertainty is a consequence of the small sample size.

The observed increase in χ_g at low temperatures, where it becomes paramagnetic, corresponds to a relatively small number of electron spins. A plot (not shown) of the reciprocal molar susceptibility vs temperature (χ_M^{-1} vs T , encompassing the 5–300 K range) yields a molar Curie constant $C_M = \chi_M T = 0.75 \times 10^{-4}$, which gives an electron spin value of 1.5×10^{-4} per carbon atom. The C_{70} plot yields a very similar number. We believe this is a foreign paramagnetic impurity (at 100 ppm) in the C_{60} sample, because (i) solid C_{60} and C_{70} are large bandgap insulators, whereas

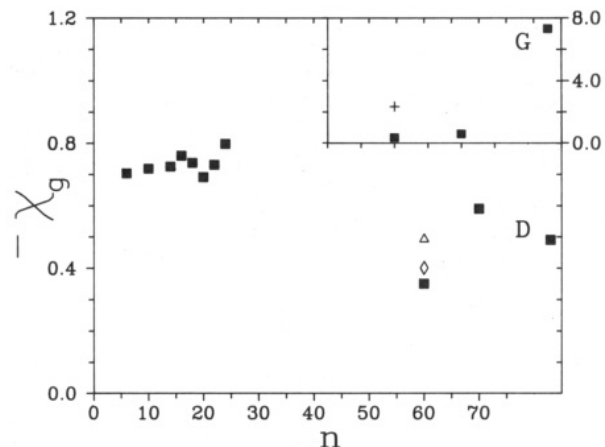


Figure 2. Comparison of the magnetic susceptibilities, χ_g in cgs units (10^{-6} cm^3), of icosahedral C_{60} to a series of aromatic hydrocarbons¹⁷ and the other allotropes of carbon (at far right, diamond D and graphite G; inset uses scale on right-hand axis).^{14,15} All values are orientationally averaged and are designated by the number of C atoms, n ; the hydrocarbons are benzene (C_6H_6), naphthalene ($C_{10}H_8$), anthracene ($C_{14}H_{10}$), pyrene ($C_{16}H_{10}$), tetracene ($C_{18}H_{12}$), perylene ($C_{20}H_{12}$), pentacene ($C_{22}H_{14}$), and coronene ($C_{24}H_{12}$). Also indicated for C_{60} are the theoretical values (+, Pauling free-electron model;¹ Δ , FLZ Hartree-Fock calculation;⁴ \diamond , estimated local contribution⁵).

(ii) the crude extract shows an EPR spectrum,¹³ and (iii) one fraction, perhaps C_{76} , is expected and indicated to be paramagnetic.¹²

The χ_g values for C_{60} and C_{70} can be compared with the analogous quantity for graphite, diamond, and aromatic hydrocarbons, as follows (see Figure 2). The relevant quantities for single-crystal graphite¹⁴ are $\chi_{\parallel} = -21.1 \times 10^{-6}$ and $\chi_{\perp} = -0.4 \times 10^{-6}$, and that for diamond¹⁵ is -0.49×10^{-6} . The C_{60} value obtained here is thus much closer to that of diamond than to the orientation-averaged value for graphite (-7.3×10^{-6}).¹⁶ Also included in Figure 2 are (orientation-averaged) χ_g values for a series of aromatic hydrocarbons which typically exceed that of C_{60} by a factor of 2 or more,¹⁷ along with the ab initio value (FLZ) and the estimated local contribution quoted by EH. It is seen that the C_{60} value (and C_{70} 's as well) lies well outside the series of aromatic molecules leading to graphite and is also somewhat below the theoretical predictions.

Discussion and Conclusions

Any interpretation of this result must take into account the electronic structure of the C_{60} and C_{70} molecules as computed earlier^{19,20} and as recently evidenced by NMR,⁸ optical,^{9,12} and photoelectron²¹ spectroscopies. These are not in disagreement with a picture in which C_{60} experiences a large resonance stabilization throughout its circuit of bonds; i.e., it is “aromatic”. Perhaps the most direct evidence is that the single ^{13}C NMR peak of C_{60} occurs at a 143.2 ppm chemical shift,⁸ which lies in the center of the aromatic region (and at the extreme lower edge of the alkene

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region).¹⁸ These considerations would argue that C₆₀ is behaving as an aromatic molecule. However, the magnitude (and sign) of χ is also ascribed in part to the "aromatic" character of carbon networks; for example, the circulation of π -electrons within layers of graphite, in response to an applied magnetic field, is evident in the difference between χ_{\perp} and χ_{\parallel} . The 20-fold smaller value found for C₆₀ clearly cannot be inferred in this way from the ¹³C chemical shift. In fact, the observed χ value ensures that an atom located at the center of the C₆₀ cage will experience minimal diamagnetic shielding.¹

In the standard picture, χ is made up of a local contribution (always strongly diamagnetic) and a nonlocal contribution (ring currents), the latter being either negative (associated with aromaticity) or positive, i.e., dominated by a Van Vleck term ("antiaromatic").^{22,23} The C₆₀ molar quantity, $\chi_M = 720 \cdot \chi_g = -250 \times 10^{-6}$, is slightly smaller in magnitude than that anticipated from local contributions alone (-291),⁵ much smaller than the Pauling free-electron model (-1681),¹ or by considering C₆₀ to be made up of 20 benzene rings, as suggested by its structure.⁵ From this point of view, the ring currents in C₆₀ are either vanishing or slightly paramagnetic.

One can understand the cancellation of the π -electron contribution by considering a Van Vleck paramagnetic term, using the calculated electronic structure of C₆₀ in conjunction with the results of recent optical measurements. The electronic structure of C₆₀ is dominated by radially directed 2p orbitals on each carbon atom. These combine into molecular orbitals in patterns that resemble the wave functions of an electron confined to reside on a spherical surface, i.e., spherical harmonics Y_{LM} of degeneracy $2(2L + 1)$,²⁰ with the filling order (I_h symmetry labels):

a_g^2	t_{1u}^6	h_u^{10}	$g_u^8 t_{2u}^6$	$g_g^8 h_g^{10}$	$h_u^{10} t_{1u}^6$
$L = 0$	1	2	3	4	5

The filled HOMO (h_u) and the LUMO (t_{1u}) are both components of the $L = 5$ complex, and crucially, they are coupled by the magnetic dipole transition operator. As such, the lowest energy excitations arising from these are optically forbidden, yet appear clearly, if weakly, in the visible spectrum (starting at 2.0 eV) through vibronic coupling, and give C₆₀ its characteristic magenta color. The T_{1g} excited state produced through this h_u - t_{1u} excitation is therefore of the character uniquely able to contribute paramagnetically to the susceptibility; the vibronic analysis of the 2.0-eV transition is consistent with an A_g -T_{1g} ($\sigma = 1$ or 2) transition,¹² so this low-lying state should be primarily responsible for a cancellation of the diamagnetic contribution. The (Van Vleck) formula representing this contribution is given by

$$\chi = \frac{2|\langle M \rangle|^2}{\Delta E}$$

where $\langle M \rangle = \langle \Psi_{A_g} | \hat{M} | \Psi_{T_{1g}} \rangle$ is the transition magnetic dipole and $\Delta E = E_{T_{1g}} - E_{A_g}$.

In the simplest calculation $\langle M \rangle = 5 \mu_B$ is assumed, i.e., carrying the full transition strength of a magnetic transition among $L = 5$ substates. With the T_{1g} state assumed to lie at $\Delta E = 2.0$ eV, this gives a paramagnetic contribution $\chi_M = +800 \times 10^{-6}$ or a

mass value $\chi_g = +1.2 \times 10^{-6}$. Comparing with Figure 2, this value is not large enough to cancel the Pauling free-electron model prediction (-2.34)¹ but is more than sufficient to cancel the ring current of 20 benzene molecules (-0.38).⁵ (C₇₀ also appears to be deficient in this respect; indeed, it is two electrons short of the 72 electrons needed to fill the $L = 5$ shell.)

Other cases have been analyzed in a manner equivalent to this, albeit without the advantage of the symmetry (pyracylene,^{3,22} the [4*n*]annulenes²³). In the case of C₆₀, the large optical gap (denominator) to the magnetic dipole coupled state is offset partly by the very large transition dipole generated by the high symmetry. Mallion³ has noted the difficulty of electronic structure calculations to correctly predict the magnetic properties of these molecules. Indeed, FLZ's results include, in contradiction to all other treatments, the t_{1u} orbital as the *second*-lowest unoccupied orbital at a high energy. Note also that our explanation differs from that given by EH¹ (decomposition into 12 five-membered rings) but attains the same paramagnetic divergence by going instead toward spherical symmetry. In this way, one obtains a situation in three dimensions (spheres) somewhat analogous to that presented in two dimensions (rings) in the [4*n*]annulenes. The ¹³C NMR result stands however in opposition to the interpretation of C₆₀ as an antiaromatic molecule. It is clear that further work will help address the "aromaticity" of C₆₀, such as calorimetric experiments to determine the resonance energy, which can in turn be related to the diamagnetic contribution. In this way, valid estimates of the separate contributions to χ might be obtained.

In conclusion, C₆₀ has been shown to have a very small diamagnetic susceptibility in comparison to aromatic molecules or graphite. The explanation given for this is unique to the electronic structure of C₆₀, so there is no reason that all other members of the fullerene series, C_{2*m*} ($m = 10, 12, 13, 14, \dots$), of which C₆₀ and C₇₀ are the 20th and 25th members, should fail to exhibit "normal" susceptibility values; in fact, because these form a homologous series ending in graphite,¹⁹ their magnetic properties must asymptotically approach those of graphite.

After this work was substantially completed, we learned that Haddon et al.²⁴ had also measured χ for C₆₀, with a value in excellent agreement with the one quoted here. They also predicted a χ for C₇₀ that is in reasonable agreement with our measurements.

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