Magnetic Susceptibility of Molecular Carbon: Nanotubes and Fullerite

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Elemental carbon can be synthesized in a variety of geometrical forms, from three-dimensional extended structures (diamond) to finite molecules (C_{60} fullerite). Results are presented here on the magnetic susceptibility of the least well-understood members of this family, nanotubes and C_{60} fullerite. (i) Nanotubes represent the cylindrical form of carbon, intermediate between graphite and fullerite. They are found to have significantly larger orientation-averaged susceptibility, on a per carbon basis, than any other form of elemental carbon. This susceptibility implies an average band structure among nanotubes similar to that of graphite. (ii) High-resolution magnetic susceptibility data on C_{60} fullerite near the molecular orientational-ordering transition at 259 K show a sharp jump corresponding to 2.5 centimeter-gram-second parts per million per mole of C_{60}. This jump directly demonstrates the effect of an intermolecular cooperative transition on an intramolecular electronic property, where the susceptibility jump may be ascribed to a change in the shape of the molecule due to lattice forces.

The discoveries of bulk C_{60} fullerite (*1*) and the related molecules known as carbon nanotubes (*2, 3*) offer a unique opportunity to study the effects of geometry on properties related to electronic structure. For example, in C_{60} fullerite, the molecular nature and curvature of the spherical molecule leads to a semiconducting energy-level spectrum; in contrast, graphite is planar and has a semimetallic band structure. A useful tool for the study of such effects is the magnetic susceptibility, χ. This bulk probe is related to the low-energy spectrum and has been used to elucidate the spectral structures of both graphite (*4*) and C_{60} (*5*). We present here results for χ in both C_{60} and carbon nanotube bundles. In C_{60}, the orientational ordering transition is found to have a marked effect on χ and thus on the intramolecular energy spectrum. In carbon nanotubes, we find a significantly enhanced susceptibility, compared to that of orientationally averaged graphite. In both cases, these results are related to novel aspects of the geometry-determined band structure.

A variety of techniques have been used to study the molecular dynamics of C_{60} fullerite. At 300 K, the crystal structure is face-centered-cubic (fcc), with an fcc lattice constant of 14.16 Å (*6, 7*). The radius of the C_{60} molecule is R_0 = 3.53 Å, implying a weakly bonded van der Waals solid. X-ray diffraction (*7*) as well as ^{13}C nuclear magnetic resonance (NMR) (*8, 9*) spectroscopy show that at high temperatures the C_{60} molecules rotate rapidly and isotropically about their positions in the lattice structure. As the material is cooled from room temperature, a first-order orientational ordering transition occurs at 260 K. At this temperature, the crystal symmetry changes to simple cubic (sc) and the lattice constant decreases on cooling by 0.044 ± 0.004 Å (*10*). The orientations of C_{60} molecules in the low-temperature ordered phase correspond to an electron-rich C=C bond on one molecule facing an electron-poor pentagon on a neighbor (*7, 11, 12*); this result suggests that Coulomb interactions drive this structural transition, consistent with the van der Waals bonding picture. Signatures of this transition have been seen in various measurements [Young's modulus (*13*), thermal conductivity (*14*), and the dielectric constant (*15*)], which are sensitive to the intermolecular spacing. In the interpretation of all of these measurements, it has been assumed that the electronic properties of the C_{60} molecule itself are invariant.

Related to the electronic structure of the C_{60} molecule is the magnetic susceptibility, χ. However, despite the trigonal bonding configuration, which is similar to that of graphite, χ for C_{60} (Fig. 1) is over an order of magnitude smaller than that for graphite. Such a small χ was predicted in a London treatment of the diamagnetic susceptibility, as discussed below. A further treatment shows that the small χ arises from the presence of both five-membered rings (5-MRs) and six-membered rings (6-MRs), which have paramagnetic and diamagnetic ring currents, respectively (*16, 17*). The near cancellation of the ring current contributions to χ is due to the unique arrangement of 5-MRs and 6-MRs that exists in C_{60}. This point is illustrated by a consideration of C_{70}, which, despite its structural similarity to C_{60}, has a χ that is larger by a factor of 2 than that of C_{60} (*18, 19*). Because undoped C_{60} is a semiconductor, there is no contribution to χ from conduction electrons, and thus χ is a good probe of the intramolecular electronic structure.

In the present study we used three different samples of C_{60}. The first was a polycrystalline sample, prepared in the usual way, purified by chromatography, and heated under vacuum to drive away residual solvent. The second sample consisted of several crystals ranging from 0.1 to 3 mm in size, prepared by a zone furnace technique (*20*). The third sample was composed of crystals that had not been exposed to the atmosphere. We measured the susceptibility using a commercial SQUID (superconducting quantum interference device) magnetometer, operating at an applied magnetic field of 0.5 T.

Figure 1 shows the temperature-dependent susceptibility, $\chi(T)$, for C_{60}, compared with that of other forms of carbon. Our value, $\chi(300) = -4.23$ centimeter-gram-second (cgs) parts per million (ppm) per mole of C [$\chi(300) = -254$ cgs ppm per mole of C_{60}], is consistent with previously reported values of $\chi(300) = -260 \pm 20$ (*18*) and -250 (*19*) cgs ppm per mole of C_{60}.

Higher resolution $\chi(T)$ values are shown in Fig. 2 for the second sample discussed above. At low temperatures, a Curie-law upturn due to 20 ppm per mole of spin-1/2 moments is observed. This small level of impurities is a feature of every carbon sample studied and is not expected to affect the bulk electronic properties. At a higher temperature, 259 K, there is a small jump with a change in susceptibility of $\Delta\chi \equiv [\chi(T > T_c) - \chi(T < T_c)]_{T \to T_c} \approx 2.5$ cgs ppm per mole of C_{60} (T_c is the critical temperature). This jump was observed and its magnitude was the same in all the samples studied.

Because $\chi(T)$ in insulating molecular solids is usually considered to be an intramolecular property, this result represents a unique situation in that an intermolecular cooperative transition is affecting the intramolecular

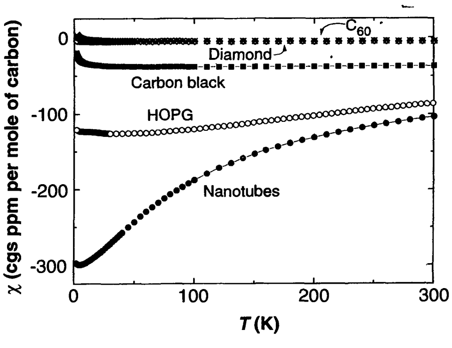

Fig. 1. Orientationally averaged magnetic susceptibility of various forms of carbon.

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energy spectrum. Other probes that are sensitive to the intramolecular spectrum do not show as marked an effect. In infrared spectroscopy studies (*21*) there is no sharp feature at T_c in vibrational-mode absorption lines at 1183 and 1430 cm^{-1}, beyond the more gradual changes associated with rotational freezing. Similarly, in Raman spectroscopy (*22*), changes in vibrational modes at 1430 and 1555 cm^{-1} occur in the vicinity of T_c, but these changes are spread over at least 40 K, in contrast to the transition width of ≈0.5 K in the present measurement. In NMR studies where the resonance frequency is proportional to the susceptibility (*23*), the frequency shift needed to observe the present $\Delta\chi$ is about 0.006 ppm, well below the sensitivity limits of solid-state NMR.

To understand better the microscopic origin of $\Delta\chi$ at the orientational ordering transition, we review the various approaches taken to calculate χ for the C_{60} molecule. The simplest approach, which treats the molecule as a structureless sphere with 60 free electrons, greatly overestimates χ. For instance, to estimate the ring current contribution χ_π, one can apply Pauling's formula for Larmor diamagnetism,

$$\chi_\pi = -60(e^2/4m_e c^2)\langle\rho^2\rangle \qquad (1)$$

where e is the electronic charge, m_e is the mass of the electron, c is the speed of light, and $\langle\rho^2\rangle = 2r^2/3 = 4.09\ell^2$ is the expectation value of the mean square radius (r^2) of the electron orbits, with bond length ℓ, as discussed by Elser and Haddon (*5*). This equation yields $\chi_\pi = -1680$ cgs ppm per mole of C_{60} to which must be added the susceptibility due to the localized electrons. Using the scheme of Haberditzl (*24*) and Dauben *et al.* (*25*) (developed for hydrocarbons) yields $\chi_{local} = -291$ cgs ppm (*25*), whereas the Hameka procedure gives $\chi_{local} = -262$ cgs ppm (*26*). An additional refinement to the localized contribution to χ may be necessary to account for the effects of strain; an estimate by Schmalz leads to a decrease in $|\chi_{local}|$ of 40 cgs ppm (*26*). Thus, the total susceptibility in the free electron treatment is $\chi \approx -2000$ cgs ppm per mole of C_{60}, which far exceeds the experimental value of $\chi = -260$ cgs ppm (*18, 19*), a value consistent with $\chi_\pi \approx 0$, given the size of χ_{local}. Such a low value was predicted by Elser and Haddon (*5*) on the basis of a London calculation of χ_π. The low χ_π value in this scheme arises from the paramagnetic (Van Vleck) contributions of the excited states, which almost completely cancel the diamagnetic contributions from the valence states. With the above values of the local susceptibility, the total susceptibility in the London treatment ranges from −215 to −414 cgs ppm (*18, 27*), which, in comparison with the experimental value, implies a vanishingly small χ_π.

To understand the change in χ observed in the experiments (Fig. 2), we must consider a refinement of the London treatment that takes into account the details of the structure of the C_{60} molecule, as discussed by Elser and Haddon (*5*). We shall consider two distinct categories of molecular distortions: those that preserve and those that disrupt the icosahedral symmetry. In the former case, it is known that an icosahedral C_{60} molecule has two different C–C bond lengths: Bonds connecting 5-MRs have $\ell_1 = 1.40$ Å, whereas those bonds that constitute the sides of 5-MRs have $\ell_2 = 1.46$ Å (*28*). The symmetry-conserving effect was considered in the original London calculation (*5, 24*), where it was noted that the expected deviation ($\ell_1 < \ell_2$), would lead to a small diamagnetic ring current contribution to the magnetic susceptibility of C_{60}. Within this framework, we calculate that the experimental bond lengths lead to $\chi_\pi = 1.69\ \chi_\pi$(benzene) ≈ −57 cgs ppm, which is in the middle of the range of values given in the original calculation (*5, 18, 27*). Furthermore, this value of the ring current susceptibility would be of about the right magnitude to account for the NMR chemical shift observed for ^3He endohedral in C_{60} (*29*) and allow for the correction due to strain in the local contribution to the susceptibility discussed above. If we then consider small additional changes to the ratio ℓ_2/ℓ_1, we find that the observed $\Delta\chi = 2.5$ cgs ppm per mole of C_{60} can be accounted for by a relative bond length change of about 0.003 Å, a value below the resolution of published results but not experimentally inaccessible.

The effect of symmetry-disrupting structural distortions are more difficult to gauge, but given the large Van Vleck paramagnetism in C_{60} (*5, 18, 19*), which is dominated by matrix elements between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (*19*), it is possible that the lower symmetry of the lattice could perturb the magnetic transition dipole moment so as to reduce the transition probability when the molecules order.

A clue to the origin of the observed $\Delta\chi$ comes from a neutron scattering study of the structural changes that occur below the orientational ordering transition (*30*). In this work it was shown that, at 5 K, there exists a range of bond lengths in the molecule, contrary to the gas-phase result of two distinct lengths. For example, ℓ_1 ranges from 1.366 to 1.412 Å and ℓ_2 ranges from 1.420 to 1.487 Å (all values ± 0.01 Å), the latter depending on whether the relevant 5-MR is facing a neighboring molecule or not. The distribution of bond lengths represents the electrostatic influence of the fcc lattice. These bond length distributions, whose widths have a precision of about two standard deviations, are consistent with symmetry-disrupting type distortions discussed above. However, a clean separation of the two modes of distortion is not possible from the data. Nevertheless, the variations in bond lengths that are discernible in the data are clearly of sufficient magnitude to account for the change in the molecular electronic structure of the molecule at the ordering transition.

Finally, we discuss the large susceptibility observed in carbon nanotubes. For the present measurements, we used material grown at Rice University according to the literature procedure (*2, 3*). Susceptibility measurements were performed as described for C_{60}. The data for the temperature dependence of χ are shown in Fig. 1, where we also show data for orientationally averaged highly oriented pyrolytic graphite (HOPG). The large diamagnetic χ in graphite is understood to arise from interband transitions, which dominate the magnetic response for this semimetal (*4*). The larger magnitude of χ for the tubes compared to graphite is surprising. We observed no dependence of χ on the orientation of the sample with respect to the magnetic field. This is not unexpected because the sample consists of many tube bundles, allowing for random orientation of individual nanotubes. Nevertheless, the large magnitude of χ strongly suggests that, in at least one of the two principal directions, either normal or parallel to the symmetry axis, χ is larger than in the similar directions in graphite. One possibility is that, because the individual nanotubes are closed structures, ring currents may flow around the

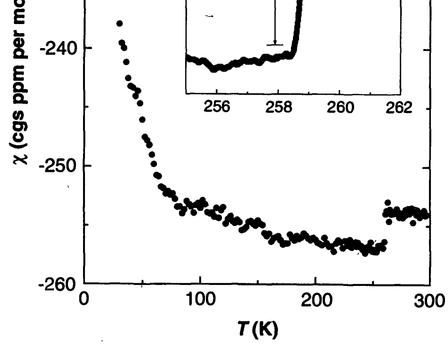

Fig. 2. Magnetic susceptibility of C_{60} as a function of temperature. The upturn at lower temperatures is due to a small impurity concentration (2×10^{-5} per mole of carbon). The jump at 259 K is expanded in the inset. No hysteresis was observed between warming and cooling to within 0.5 K.

waist of the tube in response to a field along the tube axis. In this interpretation the diamagnetism of the tubes would be greater than that of graphite because of the different current pathways provided by the two materials. In graphite, ring currents are confined to the planes and only flow when the field has a component normal to this direction.

It has been shown in band structure calculations that the electronic structure of nanotubes is highly sensitive to the degree of helicity in the carbon atom network (*31*). Three different categories of helicity are identified, each with its particular band structure. In general, however, the band gap scales with helicity, except for high-symmetry configurations. Because the interband processes that give graphite its large diamagnetism will be absent for large band gaps, it is apparent from the present data that the majority of tubes have a narrow gap band structure similar to that of graphite. Hence, the present data strongly suggest that the bulk of the nanotubes correspond to highly symmetric wrapping of graphite sheets, most likely the result of negligible helicity. However, the small spin susceptibility observed in our previous study (*32*) provides no evidence for metallic character in the nanotubes. Clearly, further work, both experimental and theoretical, is needed to resolve these issues.

Note added in proof: After submission of this work, we learned of similar studies (*33*).

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Water on Mars: Clues from Deuterium/Hydrogen and Water Contents of Hydrous Phases in SNC Meteorites

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Ion microprobe studies of hydrous amphibole, biotite, and apatite in shergottite-nakhlite-chassignite (SNC) meteorites, probable igneous rocks from Mars, indicate high deuterium/hydrogen (D/H) ratios relative to terrestrial values. The amphiboles contain roughly one-tenth as much water as expected, suggesting that SNC magmas were less hydrous than previously proposed. The high but variable D/H values of these minerals are best explained by postcrystallization D enrichment of initially D-poor phases by martian crustal fluids with near atmospheric D/H (about five times the terrestrial value). These igneous phases do not directly reflect the D/H ratios of martian "magmatic" water but provide evidence for a D-enriched martian crustal water reservoir.

The water in the present martian atmosphere is strongly enriched in deuterium relative to water on Earth, with a D/H ratio approximately five times the terrestrial value (*1*), corresponding to a δD value of +4000 (*2*). It is generally assumed that Mars and Earth originally had similar values of the D/H ratio ($\sim 1.5 \times 10^{-4}$) but that escape of hydrogen (relative to heavier deuterium) from the martian upper atmosphere throughout the planet's history has led to the observed D enrichment (*3, 4*). It may be possible to test this presumption because the D/H ratio of the martian interior has likely retained its original value. Unlike Earth with its subduction zones, on Mars recycling of near-surface and atmosphere-derived (meteoric) waters into the mantle is generally considered to be an unimportant process [(*5*) but see (*6*) for an alternative view]. Thus, a direct measurement or even an indirect inference of the D/H value of martian magmatic (interior) water could provide a fundamental constraint on the extent of hydrogen loss on Mars. Moreover, neither the abundance nor the hydrogen isotopic composition of water in the martian crust (present either as a meteoric component or in hydrogen-bearing minerals) is well characterized (*4*). However, a significant component of the martian water budget could be present in this crustal reservoir, and the determination of its D/H ratio would constrain the nature of its interaction with the atmosphere.

The 10 SNC meteorites are igneous rocks widely believed to be samples from Mars that were ejected from that planet by one or more impact events. The hypothesis of a martian origin for the meteorites is based on their young crystallization ages ($\leq 1.3 \times 10^9$ years), the close correspondence between the composition of the martian atmosphere and that of volatile components trapped in shock-derived glasses, and many other geochemical arguments (*7*). Because the SNCs are fine- to medium-grained igneous rocks that show evidence for crystal accumulation, they were probably emplaced as shallow intrusions into the martian crust or as crystal-rich surface flows (*7*). Postcrystallization alteration products that include clay minerals (*8*) show conclusively that the nakhlites (3 of the 10 SNCs) interacted with fluids in the martian crust at low temperatures after the magmas solidified. The alteration products in the nakhlites have been shown to contain water that

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