Magnetic susceptibility of carbon structures

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Measurements of the magnetic moment and susceptibility of diamond, graphite along and perpendicular to the c axis, C_{60}, and carbon nanotubes are reported as a function of magnetic field ($0 < H < 55$ kOe) and temperature ($4.5\ \text{K} < T < 310$ K). The data on C_{60} are diamagnetic, confirm previous results, and show the influence of the phase transition near 260 K. The data on the nanotubes were taken on a sample containing a distribution of tubes with diameters in the 2–10 nm range, and reveal a mostly diamagnetic behavior with a magnetic field and temperature dependence different from graphite.

INTRODUCTION

The magnetic susceptibility of the diverse forms of carbon strongly depends on the presence or absence of aromaticlike π electrons. Diamond[1] has a reported susceptibility of $\chi \approx -4.9\times10^{-7}$ emu/g, due to diamagnetic contributions from core and valence electrons, and a Van Vleck paramagnetic term. Graphite has an anisotropic diamagnetic susceptibility.[2] The susceptibility parallel to the planes is about equal to the free atom susceptibility of $\chi \approx -5\times10^{-7}$ emu/g.[3] The c-axis susceptibility of graphite is diamagnetic and very large ($\chi \approx -30\times10^{-6}$emu/g below 100 K),[2] is due mainly to free-electron contributions, and has been extensively modeled by McClure and co-workers.[4–7] It is very sensitive to the details of the band structure, and therefore to the degree of graphitization, and has been used as a tool to characterize graphitic materials.[8] The magnetic susceptibility of C_{60} ($\chi \approx -3.5\times10^{-7}$emu/g) and C_{70} ($\chi \approx -5.9\times10^{-7}$ emu/g) has been measured more recently.[9,10] Its small value compared to that of graphite ($H//c$ axis) is ascribed to an accidental cancellation between a diamagnetic and a paramagnetic term. A measurement of the susceptibility of carbon nanotubes has been mentioned in the literature,[11] but no data on the value of χ are given.

The purpose of this paper is to provide a comprehensive experimental study of the temperature and field dependence of the magnetic moment and susceptibility of these forms of carbon over the temperature range $4.5 < T < 310$ K, and the magnetic-field range $0 < H < 5.5$ T.

EXPERIMENT

We obtained a 20.0-mg type-II natural diamond crystal (Dubbledee Harris Co., Mount Arlington, NJ), two samples (71.1 mg for the measurement of the in-plane susceptibility, and 39 mg for the measurement of the c-axis susceptibility) of highly oriented pyrolytic graphite (HOPG) (A. Moore, Union Carbide), and 83.7 mg of 99.99% pure C_{60} powder (MER Corporation). Nanotubes were grown using the standard helium-arc technique[12] at 50 A and 15 V, from 99.9995% pure graphite rods (Johnson Matthey) in a turbo-pumped growth chamber under 300 torr of 6N pure He. Scanning tunnel microscope (STM) micrographs of the nanotubes are shown in Ref. 12. The central core material containing the nanotubes was scraped off, taking care not to include any graphite from the electrodes, or any material from the ring of fused carbon that surrounds the core. By gathering material from 25 growths, 28.4 mg of nanotubes were thus obtained as a first sample for susceptibility measurements, and 34.9 mg as a second sample. STM (Ref. 12) and high-resolution TEM studies reveal that the samples are a mixture of nanotubes of different diameters, in the 2–10 nm range, and contain several percent of multishell fullerene. Most of the material does consist of nanotubes or bundles of nanotubes. Scanning electron microscope (SEM) imaging was used to check the homogeneity of the material selected for this study: It is similar to that shown in the SEM image of Ref. 12, with no spatial variation across the core of the electrode, and no perceptible variation from run to run during the growth. Spectrographic analysis using a dc arc was performed on some samples, with a 10-ppm detection limit. This revealed the presence of Fe in the HOPG material at the detection limit. No metallic impurities were detected in the graphite rods used to grow the nanotubes, but the nanotube material itself contained Al, Si, and Cu near the detection limit. No analysis was done on the diamond and the C_{60} powder.

The magnetic-moment measurements were taken in a Quantum Design model MPMS magnetic properties measurement system, which has the field and temperature range mentioned in the Introduction. A lead sample was used to calibrate the instrument by measuring the critical field dependence of the superconducting transition temperature. The measurements were carried out by systematically sweeping the field from 0 to 1000 Oe with a very small step, then from 1000 to 5000 Oe with a 1000 Oe step, and finally to 55 000 Oe with a 5000-Oe step, at ten temperatures. On most samples, we also repeated the measurements below 5000 Oe at more closely spaced temperatures (40 points between 4.5 and 300 K). On the HOPG and nanotube samples, we took 300 field points at 4.5 or 5 K. The graphite and diamond samples were attached in soda straws. The C_{60} powder and nanotube samples were enclosed in gelatin capsules. As already

mentioned, two samples of nanotubes were measured, and the results were very similar. The measurements on the first sample of nanotubes were repeated with two polarities of the magnetic field, again with identical results. The background was measured separately for all samples, and subtracted from the data. In the worst cases (in-plane susceptibility of HOPG and nanotubes), the background was about 10% of the total measurement. The accuracy of the moment measurements is about a few 10^{-8} emu, so that the accuracy of the susceptibility data depends on the field at which they are reported, and will be given for each sample separately.

RESULTS

The output of the magnetometer is a measurement of the magnetic moment M versus field and temperature. We define here the susceptibility χ as $\chi = dM/dH$ (not as M/H).

For the diamond sample, the moment is linear with field at all fields, and it is temperature independent. The susceptibility is $\chi = (-4.5 \pm 0.2) \times 10^{-7}$ emu/g, measured at 4000 Oe. This is compatible with the data of Ref. 1, assuming that they have an error similar to ours. The results are shown in Fig. 1, which also summarizes the data taken on all other forms of carbon.

The moment versus field measurements taken on the graphite sample with the field parallel to the c axis are shown in Figs. 2 (at higher temperature) and 3 (at 4.5 K). Figure 2 shows good linearity of the M-H curve below 20 kOe. Deviations at higher field at 20 K are the onset of de Haas-van Alphen (dHvA) oscillations. These are better seen in Fig. 3, which also shows χ versus H at 4.5 K. The temperature dependence of χ (measured at 200 Oe, a field at which no dHvA oscillations are resolved even at 4.5 K) is shown in Fig. 1, and the data are compared to those of Ganguli and Krishnan.[2] The accuracy

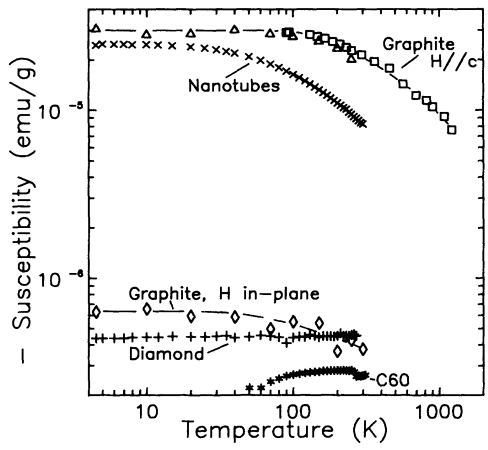

FIG. 1. Summary of the temperature dependence of the susceptibility of various carbon materials identified in the figure. The open triangles are the present data on HOPG, taken at 200 Oe, and compared to the data of Ganguli and Krishman (Ref. 2) (□). The data reported for nanotubes, graphite (H in-plane), and diamond were taken at 4 kOe, those on diamond at 8 kOe. Note that the ordinate is $-\chi$.

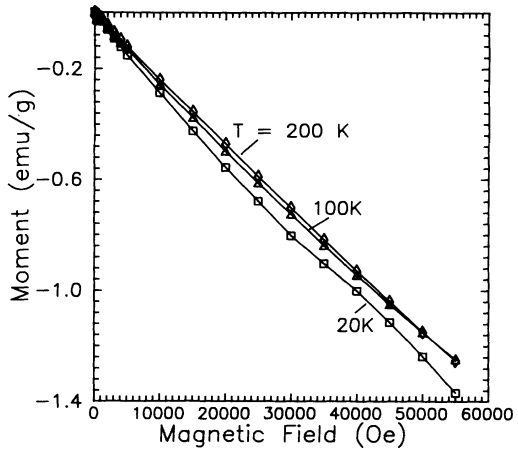

FIG. 2. Field dependence of the magnetic moment of HOPG, with the field aligned along the c axis, taken at the temperatures shown.

of these measurements is about 1%.

Figure 4 shows the moment versus field data for HOPG with the field aligned in the plane. At higher fields, the moment is diamagnetic and linear with field, and the slope is $\chi \approx -(5.5 \pm 1) \times 10^{-7}$emu/g below 20 K, and decreases to $\chi \approx -(4 \pm 1) \times 10^{-7}$emu/g at room temperature. A misalignment of less than 1° between field and the sample plane contributes to the uncertainty in this measurement. The slope, measured at 4000 Oe, is shown as a function of temperature in Fig. 1. Furthermore, the low-field dependence of the moment with field is paramagnetic, and shown in the inset of Fig. 4. The low-field ($H < 400$ Oe) susceptibility is almost temperature independent and has a value $\chi_p \approx (2.0 \pm 0.3) \times 10^{-6}$emu/g below 100 K. Above 100 K, χ_p develops a slight temperature dependence, which is smaller than the error bar, and reaches about $\chi_p \approx (2.5 \pm 0.3) \times 10^{-6}$ emu/g at 300 K. The origin of χ_p is not clear, and not likely to be due to a misalignment, since the c-axis susceptibility is strongly diamagnetic. It may be related to the presence of Fe in the sample near the 10-ppm level.

The magnetic-field dependence of the moment mea-

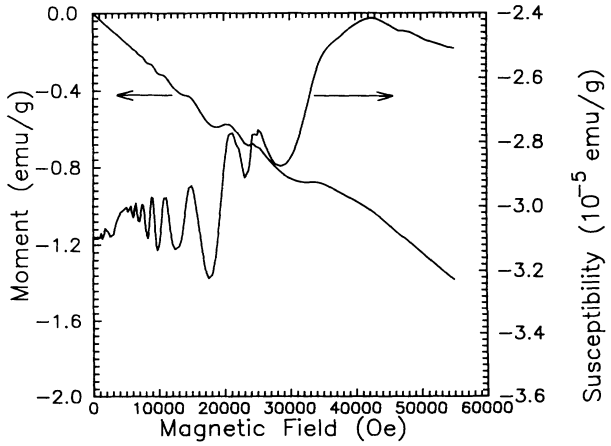

FIG. 3. Field dependence of the moment and the susceptibility at 4.5 K of HOPG, with H along the c axis.

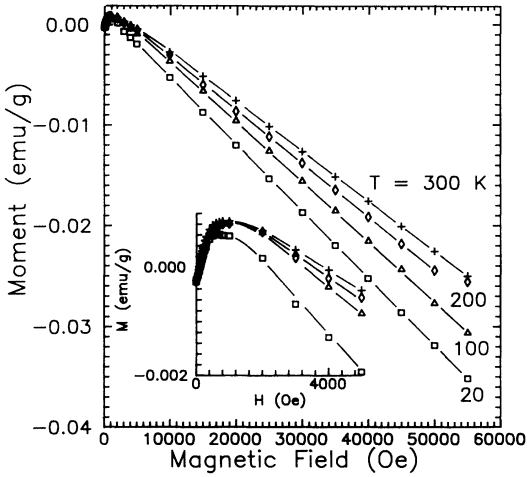

FIG. 4. Field dependence of the magnetic moment of HOPG, with the field aligned perpendicularly to the c axis, taken at the temperatures shown. The inset shows the low-field behavior magnified.

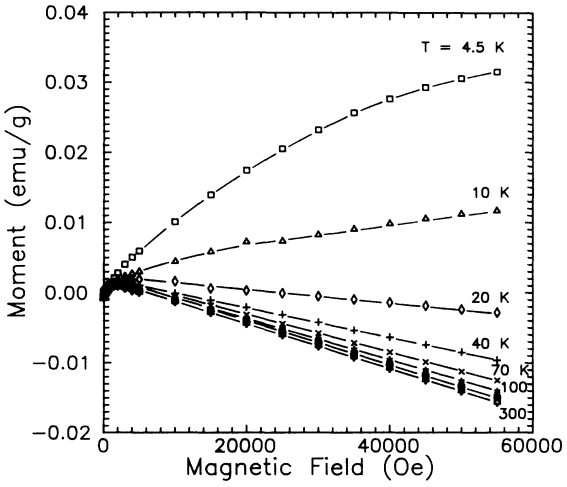

FIG. 5. Field dependence of the moment of C_{60} powder, at the temperatures shown.

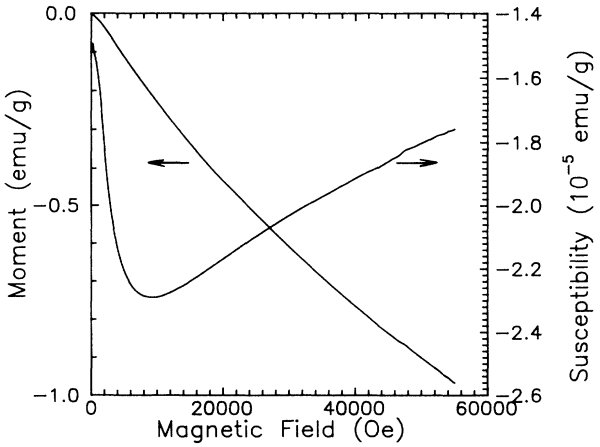

FIG. 6. Field dependence of the moment and of the susceptibility of carbon nanotubes at 5 K.

sured on C_{60} is shown in Fig. 5. The susceptibility measured at 4000 Oe is very similar to that measured by Ruoff *et al.*:[10] χ consists of a diamagnetic term $\chi_{\rm dia}$, and a paramagnetic term which follows a Curie law C_M/T. From a fit to the data, $\chi_{\rm dia} \approx -(3.1 \pm 0.2) \times 10^{-7}$ emu/g, and $C_M \approx 6.8 \times 10^{-5}$ emu K/g, which corresponds to roughly 1.4×10^{19} free spins per cm^3, or 100 ppm. This number is very close to that reported in Ref. 10, and is consistent with the nominal purity of the material. The nonlinear dependence of the moment on the field, at $H > 2000$ Oe, visible in Fig. 5 for $T = 4.5$ and 10 K, follows a Brillouin function, and has the same origin. At very low field, the moment shown in Fig. 5 is paramagnetic at every temperature, and this observation is not explained by the 100-ppm free spins. The susceptibility at 4000 Oe is shown in Fig. 1 as a function of temperature, in the range where $\chi_{\rm dia}$ dominates. There is a step in χ at 255 K, the temperature at which a phase transition is reported in the specific heat.[13]

The magnetic moment M and susceptibility $\chi = dM/dH$ of carbon nanotubes at 5 K is shown in Fig. 6, as a function of magnetic field. The moment is not

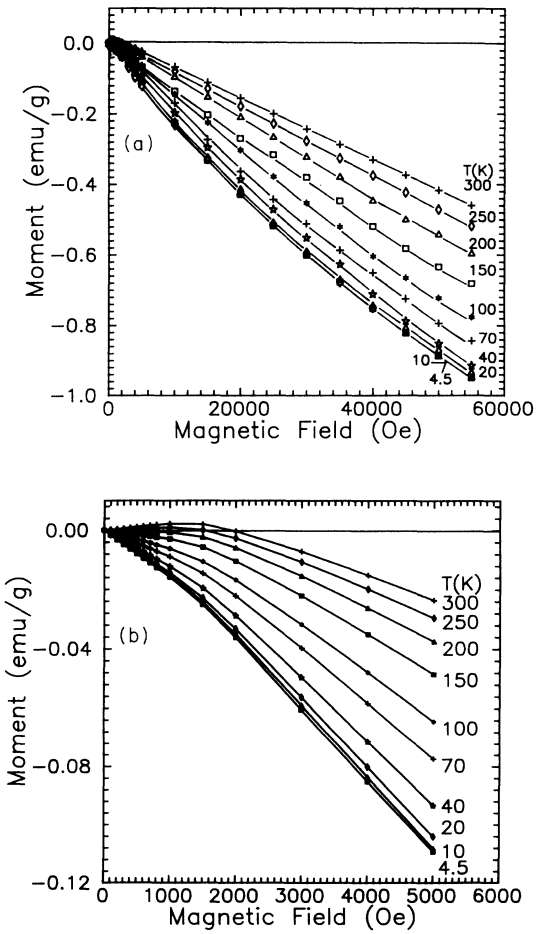

FIG. 7. Field dependence of the moment of carbon nanotubes at the temperatures shown. The high-field behavior is shown in the top frame, and the low-field behavior is magnified in the bottom frame.

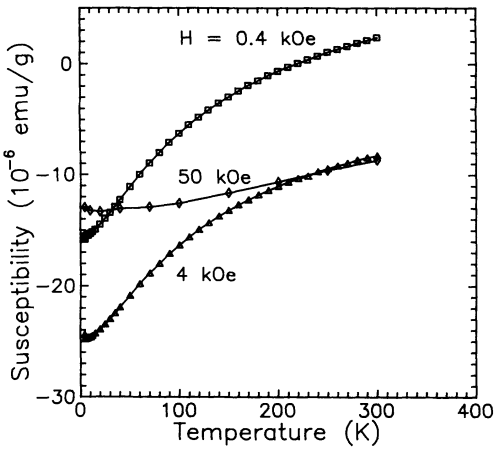

FIG. 8. Susceptibility of carbon nanotubes versus temperature at the different fields identified in the figure.

linear with field, and the susceptibility is lower than that of graphite (see Fig. 3), and has a different field dependence. The moment versus field measurements are shown for different temperatures in Fig. 7, in the high-field range in the top frame and in the low-field range in the bottom frame. The susceptibility is plotted as a function of temperature in Fig. 8, with an accuracy of about 3%. At high field, χ is diamagnetic, and has a value of about half that of graphite ($H \| c$ axis), with the same temperature and field dependence as graphite. In this field range, the magnetic length ($\sqrt{\hbar c/eH}$) is much smaller than the perimeter of the nanotubes. Therefore, the susceptibility probes only small local areas of the graphite planes, and is expected to be the geometrical average of that of rolled-up sheets of graphite. At low fields ($H \leq 400$ Oe) the magnetic length is larger than the perimeter of most tubes in the sample, and χ is a measure of the band structure of the nanotubes. Calculations of the susceptibility of nanotubes have been published:[14] the susceptibility in a perpendicular magnetic field is predicted to be the dominant term, and to be inversely proportional to the Fermi energy E_F. Even in metallic tubes, we expect that $E_F < kT$ at moderate temperatures since the overlap between conduction and valence bands has been measured to be on the order of a few meV.[15] Therefore we suggest that the strong temperature dependence of the low-field susceptibility arises from the nondegenerate nature of the carrier statistics in this regime. The susceptibility at 4000 Oe is an intermediate case and is probably sensitive to the fact that the sample consists of a distribution of tubes with different diameters.

CONCLUSIONS

The purpose of this work is to provide experimental data on the temperature and field dependence of the susceptibility of the selected carbon materials. The susceptibilities of diamond and graphite are well known and modeled. The small and nearly temperature-independent paramagnetic behavior of χ in the plane of HOPG at very low field is not quite understood, and might be an impurity effect. A similar problem was observed on the C_{60} sample. Besides that, the present data on the susceptibility of C_{60} confirm previous measurements,[10] though we observe here the influence of a phase transition at 255 K, which is not clearly visible in the previous reference, because of the coarser temperature steps used in that work. The data provided on carbon nanotubes are different from that of graphite They were acquired on a sample that contained a mixture of nanotubes of very different diameters, in the 2–10 nm range, and thus represent an average behavior. Since the free-electron contribution dominates χ in graphite materials, it is expected that these data will reveal details of the band structure of carbon nanotubes. Modeling the data is beyond the scope of this paper.

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