Novel Magnetic Properties of Carbon Nanotubes

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A magnetic field is found to have strong effects on the electronic structure and bulk properties of carbon nanotubes. A field-induced metal-insulator transition is predicted for all pure nanotubes. In a weak field, nanotubes exhibit both large diamagnetic and paramagnetic responses depending on the field direction, the Fermi energy, the helicity, and the nanotube radius. Universal scalings are found in the susceptibility as functions of the Fermi energy, the temperature, and the size of nanotubes. Comparison with recent experiments are discussed.

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The exciting discovery of carbon nanotubes [1] stimulated a large number of theoretical studies on their electronic properties. Both the tight-binding [2,3] and first principles calculations [4] predict that nanotubes can be either metallic or semiconducting depending on their helicity and size. Several recent experiments found some unusual properties. Giant magnetoresistance and indications of a field-induced metal-insulator transition are found in transport measurements [5]. Large diamagnetic susceptibilities are observed for a magnetic field both perpendicular to and parallel to the tube axis [6,7].

The magnetic properties of nanotubes were calculated by Ajiki and Ando [8] using the $\mathbf{k}\cdot\mathbf{p}$ perturbation method. However, they found that the susceptibility $\chi_\perp$ (for the field $\mathbf{H}$ perpendicular to the tube axis $\mathbf{z}$) is 3 orders of magnitude larger than $\chi_\parallel$ ($\mathbf{H}\parallel\mathbf{z}$). This result disagrees with experiments, where it is found that the two are comparable [6]. The $\mathbf{k}\cdot\mathbf{p}$ calculation is valid only if the Fermi energy is at the center of the band (half filling), and it only provides information about the band structure near the Fermi energy. For a magnetic field along the tube axis, several groups studied magnetoplasmons and persistent currents [9]. In these calculations, a free electron model on a continuous cylinder surface was used. Thus, the sensitive dependence of the band structure on the nanotube geometry was not included, and the calculated magnetic susceptibility was found to be independent of the helicity [9]. Because the orbital magnetism depends on the total band energy, it is clear that realistic calculations should include the lattice structure and the complete π band.

In this Letter we report the results of such a calculation using the tight-binding model and the London approximation. Several novel magnetic properties are found: (1) A magnetic-field-induced metal-insulator transition is predicted for all pure nanotubes, the transition depends on the helicity, the radius R, and the magnetic field direction. (2) The weak-field magnetic susceptibility is large and increases linearly with the nanotube radius R; it can be either diamagnetic or paramagnetic and is sensitive to the Fermi energy ϵ_F. (3) For each nanotube there exists a unique energy scale Δ_0, the scaled susceptibility χ/R is found to be a universal function of ϵ_F/Δ_0 and k_BT/Δ_0. (4) $|\chi|$ decreases with increasing temperature. (5) For typical nanotubes of radius $R\sim 10$ nm, $\chi\sim -300\times 10^{-6}$ cgs/mole at low temperature; it decreases to -150×10^{-6} cgs/mole at room temperature. These results are in semiquantitative agreement with recent experiments [6,7].

We use the single-orbital nearest-neighbor tight-binding Hamiltonian to calculate the band structure. A similar Hamiltonian has been used successfully for calculating the electronic structure of fullerene-related materials such as large fullerene molecules [10], the solid fullerite and fullerides [11], and nanotubes [2]. Including the effect of a magnetic field in such a model is straightforward in the London approximation. Such an approach has been used to predict the ring current, Knight shift, and the magnetic response of C_{60} and C_{70} molecules [12]. Recent NMR measurements confirm these predictions [13]. The symmetry of nanotubes was studied by several groups [2]. We follow the elegant approach of White *et al.* [3]. A nanotube is defined by a conformal mapping of a two-dimensional (2D) strip of the graphitic lattice onto the surface of a cylinder. This is characterized by a 2D lattice vector $\mathbf{L}=n_1\mathbf{a}_1+n_2\mathbf{a}_2$, where $\mathbf{a}_1,\mathbf{a}_2$ are the 2D primitive vectors of the graphite lattice and n_1,n_2 are integers. For example, the radius of the tube is $R=L/2\pi=(\sqrt{3}d_0/2\pi)\sqrt{n_1^2+n_2^2+n_1n_2}$, where d_0 is the C-C bond length. The nanotube is characterized by two symmetry operations: C_N and $S(\alpha,h)$. C_N is a N-fold rotation around the axis, where N is the largest common denominator of n_1 and n_2. The screw translation $S(h,\alpha)$ represents a rotation of α about the axis followed by a translation of h along the axis. The parameters h and α are determined from the 2D lattice vector $\mathbf{P}=p_1\mathbf{a}_1+p_2\mathbf{a}_2$, where p_1,p_2 are integers which satisfy the condition $p_2n_1-p_1n_2=N$ (for details see Ref. [3]). In the London approximation, the hopping between site i and site j is modified by a phase factor due to the presence of a magnetic field, $V_{ij}=V_0\exp[i(2\pi/\phi_0)\int_i^j\mathbf{A}(\mathbf{r})\cdot d\mathbf{r}]$. Here V_0 is the nearest-neighbor hopping amplitude, $\mathbf{A}(\mathbf{r})$ is the vector potential, and $\phi_0=hc/e$ is the flux quantum.

For the case of a uniform magnetic field **H** parallel to the tube axis **z**, both C_N and $S(\alpha,h)$ are symmetry operations. Assuming the nearest-neighbor hopping and one orbital per site, the Hamiltonian can be solved analytically to give the band structure,

$$\begin{aligned}\epsilon_n(\kappa) &= \pm V_0[3+2\cos(\delta_1)+2\cos(\delta_2)+2\cos(\delta_1+\delta_2)]^{1/2},\\ n &= 0,1,\ldots,N-1,\\ \delta_1 &= (n_1\kappa - 2\pi n p_1)/N + \beta(n_1+2n_2),\\ \delta_2 &= (n_2\kappa - 2\pi n p_2)/N - \beta(n_2+2n_1),\\ \beta &= 3d_0^2 H/4\phi_0 .\end{aligned} \tag{1}$$

Here, κ is the conjugate momentum of the screw translation $S(\alpha,h)$. Setting $H=0$ one recovers the result of White *et al.* [3].

In the case of pure nanotubes, the Fermi energy is at the center of the band, $\epsilon_F = 0$. From Eq. (1) one finds that, in addition to the dependence on the helicity and the nanotube radius, the band gap $\Delta = 2\min\{|\epsilon_n(\kappa)|\}$ varies strongly with the magnetic field. It can be shown that Δ is a simple periodic function of the flux threading the tube, $\phi = \pi R^2 H$, with a period equal to the fundamental flux quantum $\phi_0 = hc/e$. As in the case of zero magnetic field, the band gap depends on the helicity of the tube (n_1,n_2). For type I tubes, defined as those with $n_1 - n_2 = 3q$ (q an integer), the band gap is given by

$$\Delta(H) = \begin{cases} \Delta_0 \frac{3\phi}{\phi_0}, & 0 \le \phi \le \phi_0/2,\\ \Delta_0\left|3 - \frac{3\phi}{\phi_0}\right|, & \phi_0/2 \le \phi \le \phi_0 .\end{cases} \tag{2}$$

And for type II, defined as those with $n_1 - n_2 = 3q \pm 1$, the band gap is

$$\Delta(H) = \begin{cases} \Delta_0\left|1 - \frac{3\phi}{\phi_0}\right|, & 0 \le \phi \le \phi_0/2,\\ \Delta_0\left|2 - \frac{3\phi}{\phi_0}\right|, & \phi_0/2 \le \phi \le \phi_0 .\end{cases} \tag{3}$$

Here, Δ_0 is the characteristic energy associated with the nanotube. Numerical calculations show that Δ_0 is well approximated by the simple formula $\Delta_0 \approx V_0 d_0/R$.

From the above equations one can draw several conclusions: (1) In the absence of a magnetic field type I nanotubes are metallic and type II tubes are semiconducting. This agrees with previous calculations [2]. (2) In the presence of a magnetic field, a band gap is opened up in type I tubes. The gap increases with the field and reaches the maximum of $3\Delta_0/2$ at the half flux quantum. In contrast, the gap in type II tubes decreases with the field and reaches zero at one-third of the flux quantum. Thus, a magnetic-field-induced metal-insulator transition is expected for all pure nanotubes. (3) The band gap scales inversely with the tube radius R, and linearly with the magnetic flux threading the tube (see Fig. 1). (4) Because of the strong magnetic field dependence of the band structure, large magnetoresistance is expected for all carbon nanotubes. As a quantitative example, using $V_0 = 2.6$ eV and $d_0 = 1.43$ Å, we obtain $\Delta_0 = 37$ meV for a nanotube of radius $R = 10$ nm. Thus, a magnetic field of 4 T can reduce the gap of the type II nanotube from 37 meV to zero. Such a field is well within the reach of most experiments.

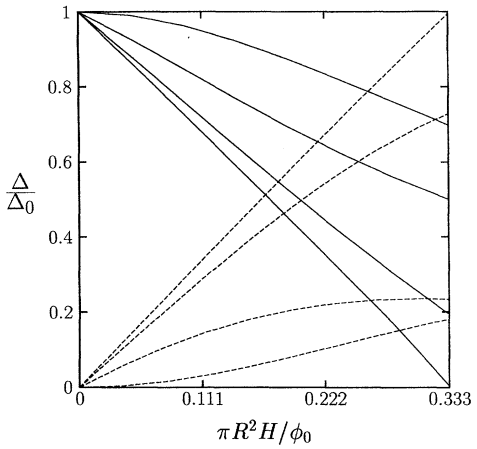

FIG. 1. The scaled energy gap Δ/Δ_0 as a function of the scaled magnetic field $\pi R^2 H/\phi_0$ for different θ, the field direction. R is the nanotube radius, $\phi_0 = hc/e$, $\Delta_0 = V_0 d_{0/R}$. Solid lines: semiconducting tubes ($n_1 - n_2 = 3q \pm 1$), $\theta = \pi/2, \pi/3, \pi/6, 0$ (top down). Dashed lines: metallic tubes ($n_1 - n_2 = 3q$), $\theta = \pi/2, \pi/3, \pi/6, 0$ (bottom up). For all figures presented in this paper we use $V_0 = 2.6$ eV, $d_0 = 1.43$ Å, thus $\Delta_0 = (3.7\text{ eV})/R(\text{Å})$.

For a uniform magnetic field making an arbitrary angle θ with the tube axis, neither C_N nor $S(\alpha,h)$ are symmetry operations. But the translation, $\mathbf{T} = [(2n_1 + n_2)/N]\mathbf{a}_1 - [(n_1+2n_2)/N]\mathbf{a}_2$, along the tube axis is a symmetry operation. Thus, one can calculate the one-dimensional band structure numerically. We find that for each family of nanotubes the reduced gap $\Delta(H,\theta)/\Delta_0$ is a universal function of the scaled magnetic field $H\pi R^2/\phi_0$, but it is no longer periodic. Shown in Fig. 1 is the field dependence for several field directions and for both types of nanotubes. The universal scaling relation enables one to estimate the band gap of any nanotube in an arbitrary magnetic field. From Fig. 1 one observes that the effect of a magnetic field is reduced when the field direction deviates from the tube axis. However, this does not imply that physical properties such as the susceptibility are less affected, as we will now discuss.

The strong field dependence of the band structure suggests a large orbital magnetic susceptibility. There are two contributions to the total susceptibility χ: the Pauli paramagnetic contribution χ_P (due to the electron spin) and the orbital term χ_{orb} (due to the change in the band energy). Our calculations show that for typical nanotubes χ_P is several orders of magnitude smaller than χ_{orb} [14]. At $T = 0$, χ (from now on refers to the orbital part only) can be calculated from the second derivative of the free

energy [15],

$$\chi = -\frac{\partial^2 F(H,T)}{\partial H^2}\Big|_{H=0},$$
$$F(H,T) = -k_B T \sum_{n,\kappa} \ln\left[1 + \exp\left(-\frac{\epsilon_n(\kappa,H) - \mu}{k_B T}\right)\right]. \quad (4)$$

Here, $\epsilon_n(\kappa,H)$ is the band dispersion. It is important to carry out the sum over the complete band as χ is calculated from the total energy. We find that contribution from far below the Fermi energy is as important as that near it. This shows that a perturbative calculation near the Fermi energy or a free electron model will not give an accurate result.

In the case of ideal carbon nanotubes at zero temperature, the Fermi energy is at the band center $\epsilon_F = 0$. We find that for $\mathbf{H} \parallel \mathbf{z}$ type I nanotubes ($n_1 - n_2 = 3q$) are paramagnetic while type II nanotubes are diamagnetic. In contrast, for $\mathbf{H} \perp \mathbf{z}$ all nanotubes are diamagnetic (Figs. 2 and 3). In all cases, χ increases linearly with the nanotube radius R and is a sensitive function of the field direction θ. Numerically the θ dependence is well approximated by the function $\chi(\theta) = a + b\cos(2\theta)$ (Fig. 2). This unusual field direction dependence can be used to separate the orbital and Pauli terms in susceptibility (the Pauli term is isotropic). It also suggests that magnetic poling is a possible method of aligning nanotubes.

Another important result we find is that χ is very sensitive to the Fermi energy, or the carrier density. In real materials, a small change in the carrier density (hence the Fermi energy) from the half filling is likely, this can lead to a large change in χ. The variation of χ with ϵ_F depends on a characteristic energy Δ_0. It is found that χ/R is a universal function of ϵ_F/Δ_0 for each family of nanotubes. Figure 3 shows scaling functions for both types of nanotubes in the vicinity of half filling. For $\mathbf{H} \perp \mathbf{z}$, χ is diamagnetic in the vicinity of the half filling, while for $\mathbf{H} \parallel \mathbf{z}$ a small deviation from the half filling changes the susceptibility dramatically. (Notice that for the type II nanotubes, the Fermi energy jumps from $\epsilon_F = 0$ to $|\epsilon_F| > 0.5\Delta_0$ for a small change in the carrier density. For a typical type I nanotube of radius $R \sim 10$ nm, the carrier density at $\epsilon_F = \pm\Delta_0$ is around 1.0 ± 25 ppm.) For the Fermi energy far away from the band center, we find that the susceptibility oscillates rapidly as a function of the Fermi energy. For a fixed ϵ_F, the susceptibility

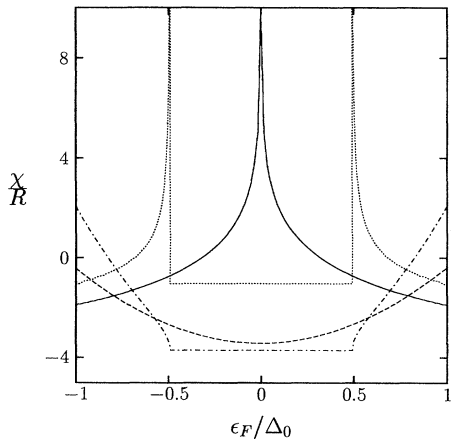

FIG. 3. Universal scaling of χ/R as functions of the scaled Fermi energy ϵ_F/Δ_0. $T = 0$. Solid line: $\mathbf{H} \perp \mathbf{z}$, $n_1 - n_2 = 3q$. Dot-dashed line: $\mathbf{H} \perp \mathbf{z}$, $n_1 - n_2 = 3q + 1$. The case of $n_1 - n_2 = 3q - 1$ is very similar to that of $n_1 - n_2 = 3q + 1$. χ/R is in units of 10^{-6} cgs/mole Å.

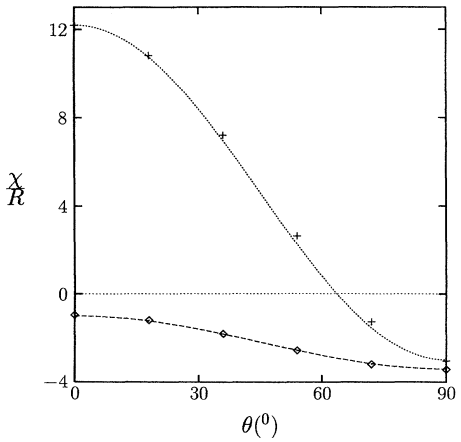

FIG. 2. The scaled susceptibility χ/R as a function of the θ. $\epsilon_F = 0$, $T = 0$. Pluses: $n_1 - n_2 = 3$. Diamonds: $n_1 - n_2 = 3q + 1$. Lines are fits using the functional form $a + b\cos(2\theta)$. The case of $n_1 - n_2 = 3q - 1$ is very similar to that of $n_1 - n_2 = 3q + 1$. χ is in units of 10^{-6} cgs/mole, R is in units of Å.

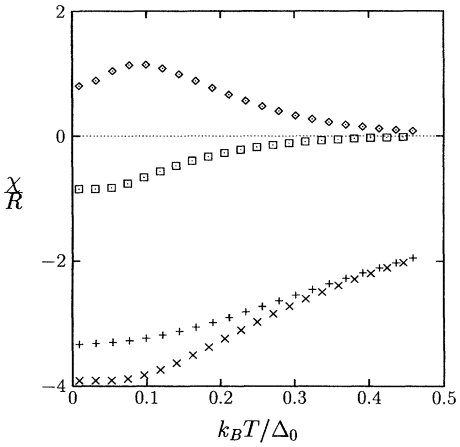

FIG. 4. The universal dependence of the scaled susceptibility χ/R on the scaled temperature $k_B T/\Delta_0$. The Fermi energy is at $\epsilon_F = 0.2\Delta_0$. Squares: $\mathbf{H} \parallel \mathbf{z}$, $n_1 - n_2 = 3q$. Diamonds: $\mathbf{H} \perp \mathbf{z}$, $n_1 - n_2 = 3q - 1$. Pluses: $\mathbf{H} \perp \mathbf{z}$, $n_1 - n_2 = 3q$. Crosses: $\mathbf{H} \perp \mathbf{z}$, $n_1 - n_2 = 3q - 1$. The case of $n_1 - n_2 = 3q + 1$ is very similar to that of $n_1 - n_2 = 3q - 1$. χ/R is in units of 10^{-6} cgs/mole Å. For a typical nanotube of radius $R = 10$ nm, the unit of χ in the vertical axis is 100×10^{-6} cgs/mole, the temperature unit is $\Delta_0/k_B = 430$ K.

also oscillates rapidly with the magnetic field in the high field limit (when the flux threading the tube is greater than the flux quantum). Such oscillations are similar to those found in continuous models [9]. Results of our high field calculations will be discussed in a separate publication.

Finally, in Fig. 4 we show the temperature dependence of orbital susceptibility. In all cases the magnitude of χ decreases with increasing T. (In contrast, the Pauli susceptibility increases with the temperature.) Universal scaling is obtained if the temperature is scaled by Δ_0. For a typical nanotube of radius $R \sim 10$ nm, $\Delta \sim 37$ meV, in a perpendicular field the calculated χ changes from -300×10^{-6} at low temperature to -150×10^{-6} cgs/mole at room temperature.

Our calculations provide a qualitative explanation for the unusual transport and magnetic properties observed in recent experiments. The large magnetoresistance observed in nanotube bundles [5] suggests that it is likely due to the sensitive dependence of the band structure on the magnetic field. If so, our calculations predict that the magnetoresistance should be also very sensitive to the field direction and the carrier density. The magnetic susceptibility was measured by two groups, one on randomly oriented carbon nanotubes [7] and the other on aligned nanotube bundles [6]. At low temperature the reported χ ranges from -200×10^{-6} to -300×10^{-6} cgs/mole. From these data and our calculations we estimate that the typical nanotube radius in those samples is around $R \sim 7$ to 10 nm, which agrees with that reported in literature. In addition, both experiments found that $|\chi|$ decreases substantially as the temperature increases [16], in agreement with our calculations.

Finally we want to point out a discrepancy between our calculations and experiments. The experiment of Wang *et al.* [6] shows that χ is more diamagnetic when $\mathbf{H} \parallel \mathbf{z}$ than when $\mathbf{H} \perp \mathbf{z}$. Our calculations predict the reverse for $\epsilon_F \sim 0$ (Fig. 3). Though it is possible to choose a ϵ_F such that our calculations agree with experiments, such a quantitative comparison should wait for better experiments and improved theoretical calculations. For example, the issue of uniformity of nanotubes should be addressed by experiments, and the fact that most nanotubes are multilayered should be included in theoretical considerations. Further experiments such as the doping dependence should provide important information for comparison.

In conclusion, we have shown that novel magnetic properties are expected for carbon nanotubes. A field-induced metal-insulator transition is predicted for all pure nanotubes. A large magnetoresistance is expected due to the sensitive dependence of the electronic structure on the external magnetic field. The weak-field magnetic susceptibility is predicted to be large and increases linearly with the nanotube radius. The susceptibility can be either diamagnetic or paramagnetic, depending sensitively on the helicity of the nanotube, the field direction, and the Fermi energy. A characteristic energy Δ_0 exists for both metallic and semiconducting nanotubes. Universal scaling is found in χ as functions of the scaled Fermi energy ϵ_F/Δ_0 and temperature k_BT/Δ_0. Both the magnitude and the temperature dependence of the susceptibility calculated are in semiquantitative agreement with recent experiments. Our results indicate that careful measurements of the magnetic susceptibility can provide an efficient probe to characterize nanotubes. The novel and unusual magnetic properties of nanotubes may have promising applications in areas such as the magnetoelectronics and the magnetic sensors.

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[16] Part of the susceptibility observed may be related to the sample quality, which may also affect the relative magnitude of $\chi_\parallel$ and $\chi_\perp$.