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LETTERS

Magnetic Orientation and Magnetic Properties of a Single Carbon Nanotube

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Carbon nanotubes were suspended in carbon tetrachloride and placed in magnetic fields of <80.0 kOe at 310 K. Scanning electron microscopy showed that a single and free nanotube was oriented with the tube axis parallel to the fields. From the Boltzmann distribution of tube directions, the anisotropy of susceptibilities parallel ($\chi_{\parallel}$) and perpendicular ($\chi_{\perp}$) to the tube axis is estimated to be $\chi_{\parallel} - \chi_{\perp} \sim (9 \pm 5) \times 10^{-6}$ emu per mole of carbon atoms ($\chi_{\perp} < \chi_{\parallel} < 0$).

1. Introduction

Carbon nanotubes are comprised of coaxial tubules of graphitic sheets; on the tubules, carbon atom hexagons are arranged in a helical fashion about the tube axis.[1,2] Nanotubes may be applied in nanometer scale engineering. Their electronic[3−6] and magnetic[7,8] properties have been of great interest in theoretical studies. Alignment of nanotubes is crucial to draw the anisotropic behavior from them.

Several methods of alignment of nanotubes have been reported: carbon arc discharge producing buckybundles;[9] clipping of epoxy resins;[10] rubbing of films;[11] chemical vapor deposition over iron embedded in mesoporous silica,[12] over porous alumina,[13,14] over cobalt etched on silica,[15] over nickel coated on glass,[16] and over iron patterned on porous silicon.[17]

The magnetic orientation provides another method of alignment of nanotubes. The orientation in magnetic fields has been investigated for paramagnetic[18] and diamagnetic[19] substances and proteins.[20−23] The orientation arises from the magnetic anisotropy energy and follows the Boltzmann distribution at thermal equilibrium.[19c] The technique can be used for nanotubes in an isolated condition, thus, possessing applicability to alignment on production and process in the gas and liquid phases.

The present paper describes the magnetic orientation of nanotubes. Preliminary work showed that, when suspended in organic solvents and placed in magnetic fields, nanotubes were oriented parallel to the fields.[24−26] The magnetic anisotropy of nanotubes is estimated from the field-intensity dependence (0.0−80.0 kOe) of orientation.

2. Experiment

Carbon nanotubes were purified as follows. Nitric acid (2.3 mol dm^{-3}) containing nanotubes (Vacuum Metallurgical, >95%) was refluxed for 24 h. The solution was cooled and diluted with deionized water. The substance was collected on a membrane filter (Nihon Millipore, JG, 0.2 μm) and washed with deionized water and ethanol (Japan Alcohol Trading, >99.0%).

Nanotubes were suspended in carbon tetrachloride (Kanto Chemical, >99.5%) by an ultrasonic homogenizer (Sine Sonic UA-100, 36 kHz, 65 W) for 2 h. For the orientation experiment on floating nanotubes, the suspension (0.20 mg cm^{-3}, 1 cm^{3}) was placed on a cover glass (18 × 18 × 0.15 mm) in a glass

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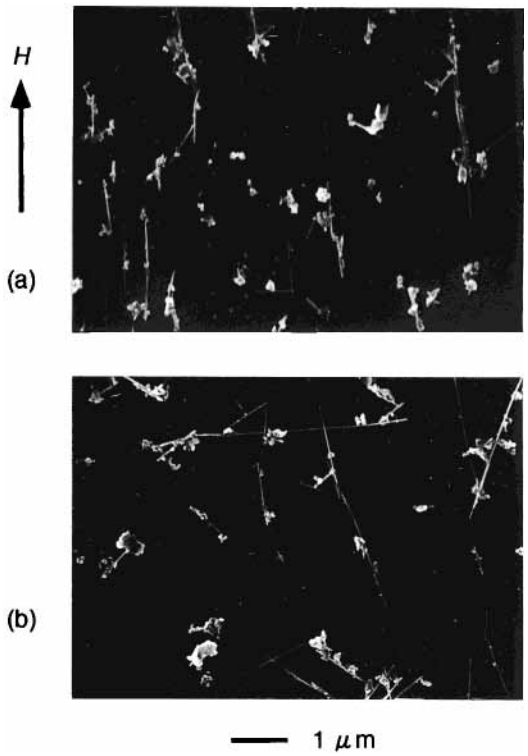

Figure 1. SEM images of carbon nanotubes suspended in carbon tetrachloride and placed in (a) 80.0 kOe and (b) zero magnetic fields. The field direction is shown with an arrow.

vessel (ϕ 30 × 15 mm) under the magnetic fields at 310 K for 4 h. The solvent was vaporized during this period. The temperature of the glass vessel was kept constant by water flow from a circulator (Advantec LP-3100). For the orientation experiment on settled-down nanotubes, the suspension was allowed to stand under zero field at 290 K for 3 h so that the supernatant became colorless. Then, it was exposed to the magnetic fields at 310 K for 4 h and the solvent was vaporized.

The magnetic fields up to 80.0 kOe were applied by using a superconducting magnet (Oxford Spectromag 1000). The field direction was horizontal.

The orientation and length of nanotubes were observed by a scanning electron microscope (SEM; JEOL JSM-5400, 30 keV). The samples were coated with gold. The observation was made for 100−180 tubes at each field intensity.

The diameter of nanotubes was measured by a field-emission transmission electron microscope (FE-TEM; Hitachi HF-2000, 200 keV). The samples were prepared on a carbon copper grid in the glass vessel.

3. Results

3.1. Orientation and Size of Carbon Nanotubes. The suspension of carbon nanotubes was placed in magnetic fields, and the solvent was vaporized. The orientation was observed by SEM. In Figure 1a is shown the SEM image of nanotubes at an 80.0 kOe field. They are 1.5 ± 0.6 μm in length, and oriented with the tube axis parallel to the field. Spherical regions seem to be amorphous graphitic nanoparticles produced as byproducts in carbon arc discharge. In Figure 1b is shown the SEM image of nanotubes at zero field. They are oriented randomly.

The experiment was made to resolve whether nanotubes were rotated after they settled down on the bottom. The suspension of nanotubes was allowed to stand at zero field, until the supernatant became colorless. Then, it was exposed to an 80.0 kOe field and the solvent was vaporized. In the SEM image, nanotubes are oriented parallel to the field. This shows that they are rotated even after settling down.

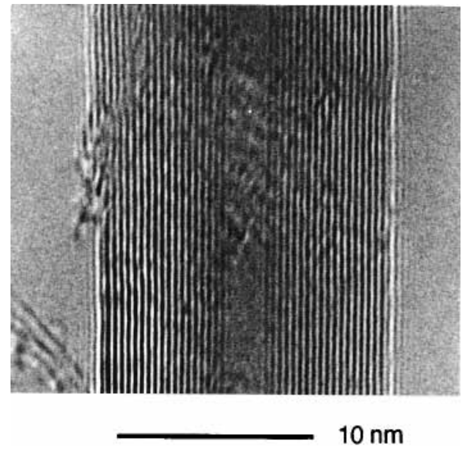

Figure 2. TEM image of carbon nanotube suspended in carbon tetrachloride.

The structure of nanotubes was observed by TEM (Figure 2). The outermost and innermost tubules are 17.9 ± 4.4 and 2.8 ± 1.2 nm in diameter, respectively. The wall thickness is 23 ± 7 sheets, and the intershell distance is 0.349 ± 0.005 nm, which agrees with the reported value of 0.344 nm.[27]

3.2. Distribution of Directions of Carbon Nanotubes. Carbon nanotubes were placed in magnetic fields of various intensities (0.0−80.0 kOe). The directions of tube axes were measured by SEM. The distribution of directions is shown in Figure 3. At zero field, the directions of nanotubes are random. As the field intensity increases, the proportion of nanotubes increases near the orientation that the tube axis is parallel to the field ($\theta = 0$) and the width of distribution narrows near the parallel orientation to the field. At an 80.0 kOe field, most of nanotubes are oriented parallel to the field.

4. Discussion

4.1. Magnetic Orientation. The magnetic orientation of carbon nanotubes is explained by the susceptibility anisotropy.[19c] They are magnetically symmetric along the tube axis and possess molar susceptibilities parallel ($\chi_{\parallel}$) and perpendicular ($\chi_{\perp}$) to it. The magnetic energy of nanotubes composed of mole number n of carbon atoms in a field H is expressed by

$$E(\theta, H) = -(nH^2/2)\,[\chi_{\perp} + (\chi_{\parallel} - \chi_{\perp})\cos^2\theta] \quad (1)$$

where θ is the angle between the tube axis and field H. The magnetic orientation occurs so that the energy $E(\theta, H)$ is a minimum. Experimentally, nanotubes were oriented with the tube axis parallel to the field H ($\theta = 0$). Because they are considered to be diamagnetic at ∼310 K, this requires a condition of $\chi_{\perp} < \chi_{\parallel} < 0$.

4.2. Boltzmann Distribution. The field-intensity dependence of the orientation of carbon nanotubes is interpreted as the Boltzmann distribution for the directions of different magnetic energies.[19c] The magnetic energy is minimized and nanotubes are stabilized in the direction where the tube axis is parallel to the field H ($\theta = 0$). When the field intensity is low, the difference in magnetic energy is small between any direction (θ) and the stable direction ($\theta = 0$) and the orientation is disordered to be random by the thermal energy. As the field intensity increases, the difference becomes larger between them and the probability of orientation becomes higher in the stable direction.

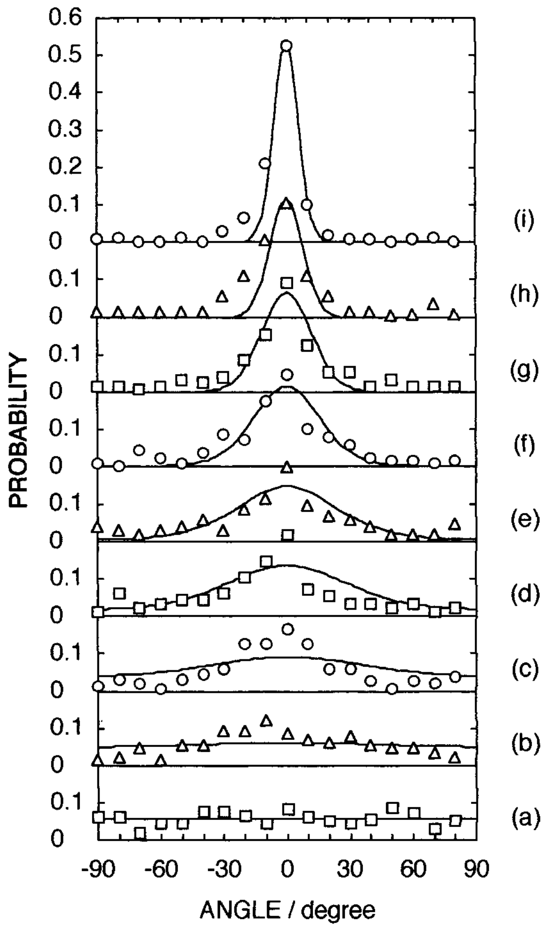

Figure 3. Observed (circles, triangles, and squares) and calculated (curves) distribution charts for the directions of carbon nanotubes in magnetic fields. The abscissa represents the angle between the tube and field. The ordinate shows the proportion of tubes directed to each angle. Field intensity: (a) 0.0, (b) 5.0, (c) 10.0, (d) 16.0, (e) 20.0, (f) 30.0, (g) 40.0, (h) 60.0, and (i) 80.0 kOe.

Nanotubes were rotated even after settling down on the bottom. They will not be subject to the friction from the glass surface, because they are light owing to the buoyancy from the solvent. The reasonable approximation is that nanotubes are placed in the horizontal plane and affected by the field H. When the tube axes and field H lie in the two-dimensional plane, the tube directions are specified by the rotation angle θ about the normal to that plane.

In the thermal-equilibrium condition at temperature T, the directions of nanotubes follow the Boltzmann statistics, and the probability of existence of nanotubes between the angles θ and $\theta + \mathrm{d}\theta$ is written as

$$P(\theta, H)\,\mathrm{d}\theta = \frac{\exp[-E(\theta, H)/kT]\,\mathrm{d}\theta}{\int_0^{\pi} \exp[-E(\theta, H)/kT]\,\mathrm{d}\theta} \qquad (2)$$

with k being the Boltzmann constant. Then the simulation can be made using eqs 1 and 2 as functions of the variables θ and H. The overall susceptibility anisotropy $n(\chi_{\parallel} - \chi_{\perp})$ is the only parameter involved in eqs 1 and 2 and determined by the simulation. It is assumed to be independent of the field intensity (5.0−80.0 kOe). The calculated distribution is also shown in Figure 3. The simulation reproduces the experimental results well, and the overall susceptibility anisotropy is estimated to be $n(\chi_{\parallel} - \chi_{\perp}) = (6.5 \pm 1.9) \times 10^{-22}$ emu.

4.3. Magnetic Anisotropy. The susceptibility anisotropy of carbon nanotubes is estimated from the magnetic orientation. Nanotubes used in the experiment have the overall susceptibility anisotropy of $n(\chi_{\parallel} - \chi_{\perp}) = (6.5 \pm 1.9) \times 10^{-22}$ emu. They are 1.5 ± 0.6 μm in length and consist of 23 ± 7 sheets. The outermost and innermost tubules are 17.9 ± 4.4 and 2.8 ± 1.2 nm in diameter, respectively. The intershell distance is 0.349 $\pm$ 0.005 nm. In graphite, the C−C bond length is 0.142 nm.[27] On the assumption that the concentric tubules have uniform length within the tube, the susceptibility anisotropy of nanotubes is estimated to be $\chi_{\parallel} - \chi_{\perp} = (9 \pm 5) \times 10^{-6}$ emu mol^{-1} (per mole of carbon atoms).

The anisotropic susceptibilities of nanotubes might be predicted from those of graphite. The susceptibilities of graphite parallel ($\chi^{G}{}_{c}$) and perpendicular ($\chi^{G}{}_{ab}$) to the c axis were reported to be $\chi^{G}{}_{c} = -253 \times 10^{-6}$ and $\chi^{G}{}_{ab} = -6 \times 10^{-6}$ emu mol^{-1} at 298 K.[28] The susceptibilities of nanotubes might be given, because of the cylindrical geometry, by $\chi_{\parallel} = \chi^{G}{}_{ab} = -6 \times 10^{-6}$ and $\chi_{\perp} = (\chi^{G}{}_{c} + \chi^{G}{}_{ab})/2 = -130 \times 10^{-6}$ emu mol^{-1}, leading to a prediction of the anisotropy of $\chi_{\parallel} - \chi_{\perp} = 124 \times 10^{-6}$ emu mol^{-1}. The magnitude of anisotropy estimated from the magnetic orientation is smaller compared to the one from the graphite structure. A possible explanation is that, because nanotubes are of closed structure, a ring current flows around the tube waist in response to fields along the tube axis.[29] In this interpretation, the diamagnetism of nanotubes parallel to the tube axis is of greater magnitude than that of graphite perpendicular to the c axis.

The anisotropic susceptibilities of nanotubes were calculated theoretically. The susceptibility perpendicular to the tube axis was found to be 3 orders of magnitude as large as the one parallel to the tube axis at 0 K: $\chi_{\perp} \sim 10^{3}\chi_{\parallel}$.[7] For typical nanotubes with diameters of 20 nm, the susceptibilities were calculated to be $\chi_{\parallel} \sim 0$ and $\chi_{\perp} \sim -150 \times 10^{-6}$ emu mol^{-1} at $\sim$300 K.[8] The sign of anisotropy obtained in the orientation experiment is consistent with the one in the theoretical calculations.

The anisotropic susceptibilities of aligned nanotubes were measured by a superconducting quantum interference device (SQUID) magnetometer. Alignment was made by production of bundles,[9] by rubbing of films,[11] and by exposure to magnetic fields.[24] The reported values are $\chi_{\parallel} = -129 \times 10^{-6}$ and $\chi_{\perp} = -115 \times 10^{-6}$ emu mol^{-1} ($\chi_{\parallel} - \chi_{\perp} = -14 \times 10^{-6}$ emu mol^{-1}) at $\sim$300 K, 5 kOe;[9] $\chi_{\parallel} = -98 \times 10^{-6}$ and $\chi_{\perp} = -62 \times 10^{-6}$ emu mol^{-1} ($\chi_{\parallel} - \chi_{\perp} = -36 \times 10^{-6}$ emu mol^{-1}) at $\sim$270 K;[11] and $\chi_{\parallel} = -96 \times 10^{-6}$ and $\chi_{\perp} = -114 \times 10^{-6}$ emu mol^{-1} ($\chi_{\parallel} - \chi_{\perp} = 18 \times 10^{-6}$ emu mol^{-1}) at 300 K, 10−20 kOe.[24] With respect to the sign of anisotropy, the orientation observation is in contrast to two of the SQUID measurements[9,11] and in agreement with one of them.[24]

In addition, it should be noted that the orientationally averaged susceptibility of nanotubes was measured by a SQUID magnetometer. The reported values are $(\chi_{\parallel} + 2\chi_{\perp})/3 = -105 \times 10^{-6}$ emu mol^{-1} at $\sim$300 K, 5 kOe[29] and $(\chi_{\parallel} + 2\chi_{\perp})/3 = -98 \times 10^{-6}$ emu mol^{-1} at $\sim$300 K, 4 kOe,[30] which are of larger magnitude than the graphite value of $(\chi^{G}{}_{c} + 2\chi^{G}{}_{ab})/3 = -88 \times 10^{-6}$ emu mol^{-1} at $\sim$298 K.[28]

The orientation observation is contradictory to the two SQUID measurements. First, whether nanotubes are isolated or not should address the discrepancy. The orientation experiment was performed for a single nanotube, which was free and separated from the others in the suspension by sonication. The two SQUID measurements were done for bundles and films, in which nanotubes were not aligned perfectly and made a loop by local connection. When a diamagnetic current is induced and circulated around the loop against fields, the susceptibilities would be estimated much differently from those of the isolated condition.[11] Second, the field dependence of susceptibilities should be included in the interpretation. The orientation experiment was examined at high fields (5.0−80.0 kOe). In the high field range (5−80 kOe), the susceptibilities probe a local area of the graphitic plane and are given approximately by the geometrical averages of those of the graphitic roll-up sheet.[30] The two SQUID measurements were made at low fields (∼5 kOe). In the low field range (<5 kOe), the susceptibilities measure the band structure of nanotubes, sensitive to the helicity and diameter, and would exhibit much different response from those of high fields.[8,30]

5. Conclusion

Carbon nanotubes were oriented parallel to an 80.0 kOe magnetic field at 310 K. The observation shows that the susceptibility parallel to the tube axis is larger than the one perpendicular to the tube axis: $\chi_{\perp} < \chi_{\parallel} < 0$.

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