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Estimation of Magnetic Susceptibility Anisotropy of Carbon Nanotubes Using Magnetophotoluminescence

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ABSTRACT

We have carried out a magnetophotoluminescence excitation spectroscopy study on micelle-suspended single-walled carbon nanotubes in high magnetic fields. By analyzing field-dependent spectral changes, we determined the degree of magnetic alignment of the observed semiconducting nanotubes at 45 T. This, together with an independently measured length distribution of the nanotubes, allowed us to estimate the magnitude of the magnetic susceptibility anisotropy $\chi_{\parallel} - \chi_{\perp}$ to be $\sim$1.4 $\times$ 10^{-5} emu/mol for 1-nm-diameter semiconducting nanotubes.

Single-walled carbon nanotubes (SWNTs), either metallic or semiconducting, are predicted to possess novel magnetic properties.[1−3] For example, while a field applied parallel to the tube axis modifies the band structure through the Aharonov-Bohm (AB) phase, leading to a logarithmically divergent paramagnetic susceptibility for metallic tubes, a perpendicular field is predicted to induce lattice instability and distortion. At low magnetic fields ($\phi \ll \phi_0$, where ϕ is the magnetic flux threading the tube and $\phi_0 = h/e$ is the magnetic flux quantum), semiconducting SWNTs are predicted to be diamagnetic both in the tube axis direction and in the perpendicular direction, with the diamagnetic susceptibility in the perpendicular direction $\chi_{\perp}$ being more negative than the susceptibility in the axial direction $\chi_{\parallel}$ while metallic SWNTs are predicted to be paramagnetic in the tube axis direction and diamagnetic in the perpendicular direction. This suggests that both semiconducting and metallic SWNTs should align in a magnetic field.

Early experimental results probing diamagnetic anisotropy performed on multiwalled carbon nanotubes (MWNTs)[4−6] showed that $|\chi_{\perp}| < |\chi_{\parallel}|$, in striking disagreement with the predictions. Later work on MWNTs[7−9] showed agreement with $|\chi_{\perp}| > |\chi_{\parallel}|$; Kotosonov[8] argues that the previous work was flawed by inaccurate estimation of nanotube orientations in the samples used. Further evidence of anisotropic magnetic susceptibilities was demonstrated through magnetic alignment of MWNTs[7,10,11] and SWNTs.[12,13] Fujiwara et al.[14,15] used magnetic alignment of MWNTs suspended in solutions to obtain the degree of diamagnetic anisotropy in individual MWNTs.

We have recently demonstrated magnetic alignment of SWNTs of specific chiralities.[16] As the magnetic field increased, absorption and photoluminescence (PL) spectra showed changes in accordance with the magnetic alignment and the predicted changes on their electronic structure due to the AB effect.[17,18] In this work, such measurements were used in conjunction with atomic force microscopy (AFM) measurements to provide the first experimental estimates on the diamagnetic anisotropy $\chi_{\parallel} - \chi_{\perp}$ of individual semiconducting SWNTs.

SWNTs were suspended in 1 wt. % sodium dodecyl sulfate (SDS)/D_2O solution following the method described in ref 19. Resulting samples were rich in individual nanotubes surrounded by SDS micelles and thus separated from other nanotubes in the solution. The PL excitation (PLE) spectrum of such samples showed peaks assigned[20] to specific nanotube species (chiralities). As a reference, 1 wt. % SDS/D_2O solution without nanotubes was used. PLE measurements were made in the Voigt geometry inside a 45 T magnet. A continuous-wave Ti:sapphire laser was used for excitation, and a liquid nitrogen cooled InGaAs detector recorded a PL spectrum for each excitation wavelength used. All measurements were done at room temperature.

Figure 1A shows a 0-Tesla PLE spectrum with chirality assignments[20] noted. The measured PL intensity (after taking into account the wavelength dependence of the excitation

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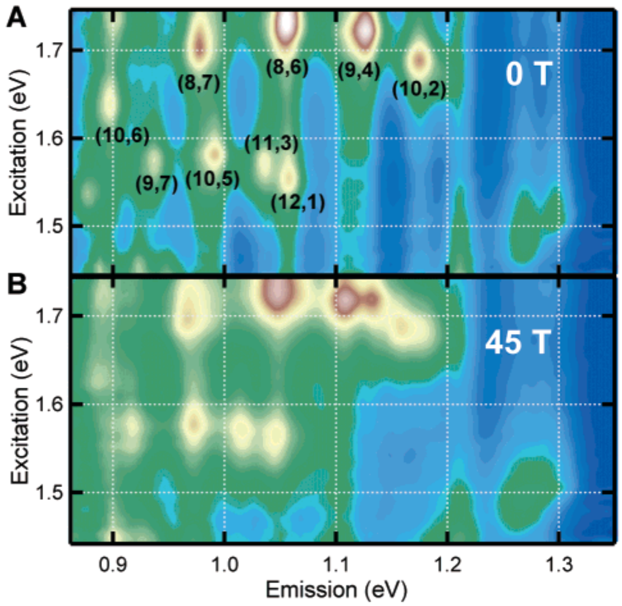

Figure 1. Photoluminescence excitation spectra of SWNT sample taken at (A) 0 T (assigned chiralities of the most pronounced peaks are noted) and (B) 45 T.

power and the detector sensitivity) is plotted as a simultaneous function of excitation photon energy (*y*-axis) and emission photon energy (*x*-axis). The 45-Tesla PLE spectrum taken for the same sample under the same conditions is shown in Figure 1B. Magnetic field induced red shifts, peak broadenings, and splittings are clearly visible.

Following the method described in ref 16, these changes can be explained as a combined result of magnetic alignment and the AB effect. The AB-effect-induced Ajiki−Ando splitting causes each PL peak to split into two peaks separated by

$$\Delta E_{AA} \equiv 6E_g\phi/\phi_0 \tag{1}$$

where E_g is the zero-field band gap.[17,18] Equation 1 is valid for $\phi/\phi_0 < 1/6$. The probability density that a given nanotube consisting of N moles of carbon is at an angle θ relative to B is

$$\frac{dP(\theta)}{d\theta} = \frac{\exp(-u^2 \sin^2 \theta) \sin\theta}{\int_0^{\pi/2} \exp(-u^2 \sin^2 \theta) \sin\theta \, d\theta} \tag{2}$$

where

$$u \equiv \{B^2N(\chi_{\parallel} - \chi_{\perp})/k_BT\}^{1/2} \tag{3}$$

and $\chi_{\perp}$ and $\chi_{\parallel}$ are perpendicular and parallel diamagnetic susceptibilities per mole of C atoms.

Figure 2 shows PL spectra for laser excitation at 795 nm. The 0-Tesla spectrum is fitted using Lorentzian peaks (lower dashed line). Terms u and ΔE_{AA} were used as fitting parameters for each peak, and for each choice of these parameters, a 45-Tesla spectrum was calculated using eqs 1 and 2. The relative amplitude between split PL peaks was obtained through the Boltzmann factor. The parameters were varied until the best agreement of the simulated (dashed curve) and measured (solid curve) 45-Tesla spectra in Figure 2 was achieved. This method gave a best-fit value $u \sim 2$ for all four main peaks in Figure 2. For comparison, a simulated 45-T spectrum assuming no magnetic alignment is shown (middle dashed line in Figure 2), which does not agree with the experimental spectrum at all, indicating that magnetic alignment is crucial for explaining the data.

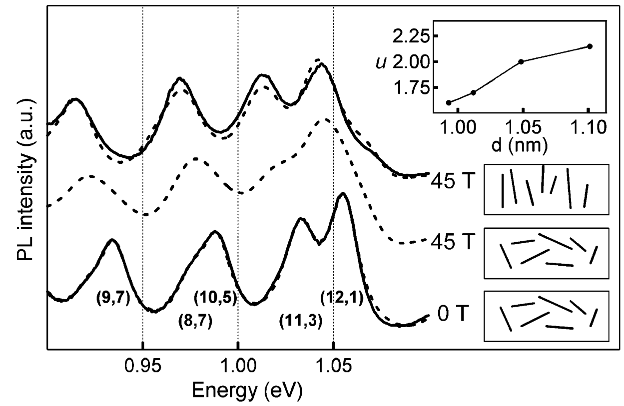

Figure 2. 795 nm excitation PL spectra (solid lines) and simulated spectra (dashed lines) at 0 T and 45 T. The inset shows extracted value for u for the four most pronounced peaks vs the tube diameter d. The middle dashed line shows the result of a simulation when there is no alignment present.

To use the determined value of u to estimate the magnetic susceptibility anisotropy using eq 3, the length distribution of the nanotubes was measured. The nanotubes were deposited onto a SiO_2 covered wafer by simply dipping the wafer into the sample solution 5−10 times. The wafer was then rinsed and imaged using an AFM. The obtained length histogram had a maximum at about 300 nm. Using this value, together with the corresponding nanotube diameter $d \sim 1$ nm, for all the four peaks, eq 3 yields $\chi_{\parallel} - \chi_{\perp} \sim 1.4 \times 10^{-5}$ emu/mol, similar to the predicted values, i.e., 1.9×10^{-5} emu/mol[1] and 1.5×10^{-5} emu/mol.[2] Furthermore, the extracted values for u show that tubes of larger diameters d align better (see the inset in Figure 2), which is in qualitative agreement with the prediction, i.e., $|\chi_{\parallel} - \chi_{\perp}| \sim d$.[1,2]

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