Magneto-optical spectroscopy of excitons in carbon nanotubes

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We describe recent results of optical experiments on single-walled carbon nanotubes in high magnetic fields, probing the influence of a tube-threading magnetic flux on their band structure and excitonic states. The magnetic flux breaks the time-reversal symmetry and thus lifts the K-K' valley degeneracy, and the amount of state splitting is determined by the Aharonov-Bohm phase. We show experimental evidence that this field-induced symmetry breaking overcomes the Coulomb-induced exciton splitting which is predicted to make the lowest singlet exciton state optically inactive (or "dark"). Thus, a magnetic field applied parallel to the tube axis "brightens" the dark exciton, resulting in a drastic increase in photoluminescence intensity with magnetic field. We also find that the amount of brightening increases with decreasing temperature.

1 Introduction

One-dimensional (1-D) excitons have been the subject of numerous theoretical studies over the last several decades. Their properties are predicted to differ significantly from excitons in higher dimensions. The exciton binding energy becomes infinite in an ideal 1-D system [1, 2] and the Sommerfeld factor, the ratio of the exciton continuum to the free electron-hole pair above the band edge, is expected to be less than 1 in 1-D semiconductors [3]. Although various low-dimensional systems have been examined experimentally, the distinct characters of 1-D excitons have not been fully revealed. Recently, excitons in single-walled carbon nanotubes (SWNTs) have emerged as an ideal candidate for exploring 1-D exciton physics due to their extreme quantum confinement with the resultant huge binding energies as well as their relatively low degrees of disorder. Recent two-photon fluorescence studies [4, 5] convincingly demonstrated the excitonic nature of interband optical processes in semiconducting SWNTs, consistent with recent theories [6-16]. These theoretical studies have not only confirmed earlier predictions for 1-D excitons in general but also raised an array of issues and questions specific to SWNT excitons, including environmental effects, the stability of excitons in metallic SWNTs, and the existence of "dark" excitons.

An optically inactive, or dark, exciton state arises due to K-K' Coulomb mixing [9,10,13-16] and could explain experimentally-observed low quantum efficiencies. A magnetic field (B) can

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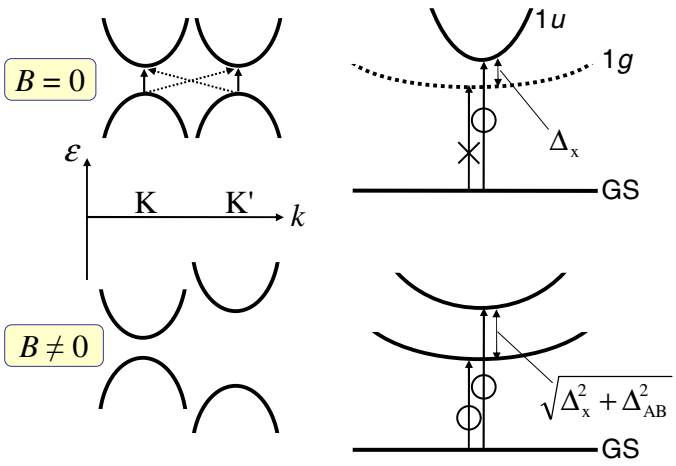

Fig. 1 The expected magnetic-field evolution of K-K' intervalley mixing and splitting in a single-particle picture (left) and an excitonic picture (right). $1u$ ($1g$) is the bonding (anti-bonding) superposition state of the K and K' exciton states. The solid (dashed) line represents a bright (dark) exciton state. Δ_x: Coulomb-induced splitting; Δ_{AB}: Aharonov-Bohm-induced splitting. Both states become optically-allowed in a magnetic field, suggesting 'magnetic brightening' of the $1g$ state.

provide insight into this problem by lifting the K-K' degeneracy in a controllable manner. Figure 1 schematically shows the influence of an applied parallel B on the Coulomb mixing among the lowest-energy singlet exciton states. In the presence of time-reversal symmetry, the lowest two exciton states are the bonding-like and anti-bonding-like linear combinations of the K-point and K'-point exciton states, which are expected to split by an amount Δ_x determined by the strength of the electron-hole exchange interaction, the tube diameter, and the dielectric constant of the surroundings [13]. The higher (lower) state is predicted to be bright (dark). When a B is applied, the K-K' degeneracy is lifted, with the amount of single-particle state splitting (Δ_{AB}) determined by the Aharonov-Bohm phase $2\pi\phi/\phi_0$ [17, 18], where ϕ is the magnetic flux threading the tube and ϕ_0 is the magnetic flux quantum. As B (and thus ϕ) increases, the relative importance of the Coulomb mixing gradually decreases. At high enough B where $\Delta_{AB} \gg \Delta_x$, both states become bright and two peaks with an equal oscillator strength are expected. In addition, the center-of-mass effective mass of the upper (lower) exciton state is expected to become heavier (lighter) with B, as also schematically depicted in Fig. 1.

Previous room temperature magneto-optical studies [19, 20, 21] on individualized SWNTs in solutions using high DC (pulsed) magnetic fields up to 45 T (75 T) revealed field-induced optical anisotropy and spectral shifts and splittings in absorption and photoluminescence (PL) spectra. Quantitative analyses, including the Aharonov-Bohm phase and magnetic alignment, showed excellent agreement with existing theory [11, 17], providing the first experimental evidence for the influence of the Aharonov-Bohm phase on the electronic states of SWNTs. In particular, it was shown that in high enough B there are two equally-bright exciton states [21]. However, the expected 'magnetic brightening' process (shown in Fig. 1) was not clearly observed. Here we present results of more recent magneto-optical experiments on carbon nanotube film samples at low temperatures in pulsed high magnetic fields.

2 Experimental Methods

2.1 Sample Preparation

Stretch aligned films of HiPco SWNTs (HPR 104) suspended in sodium dodecyl benzene sulphonate (SDBS) and bovine gel were used for these experiments. First, nanotubes were dispersed in SDBS using standard techniques [22]. Then, following a procedure developed by Kim et al. [23], the decanted sample was mixed with gelatin and cast in a thin film. After thorough drying, this film was soaked in alcohol to soften it for stretching. The film was pulled to a draw ratio of 2:1 and polarized absorption measurements were made (see Fig. 2).

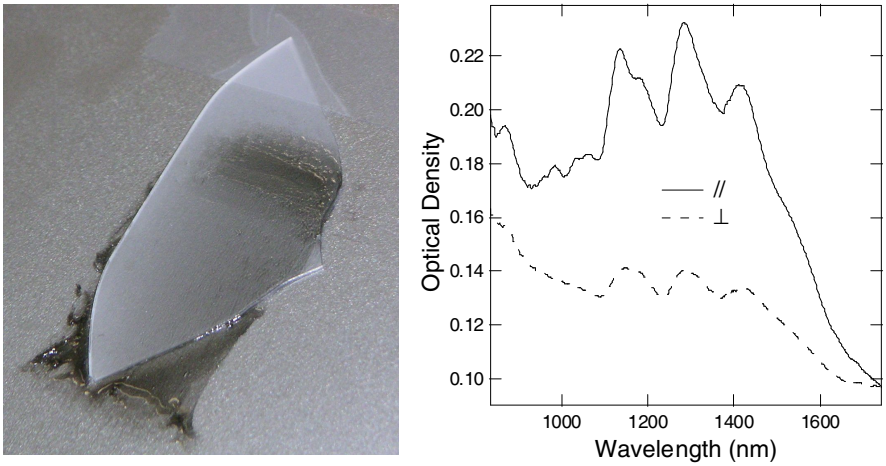

Fig. 2 Stretch aligned SWNT gel film (left) and its anisotropic optical absorption spectra (right).

2.2 High-Field Magneto-Photoluminescence Measurements

The film samples were loaded into a fiber coupled reflection PL sample probe for measurements with an excitation wavelength of 780 nm in the Voigt geometry (light propagation vector perpendicular to applied B field) from 800 nm to 1500 nm. The film orientation was such that the alignment of the nanotubes was parallel to the applied B field in order to maximize the amount of flux threading the nanotubes. Spectra were collected from 5 K to 275 K and 0 T to 56 T with a Roper InGaAs diode array. Magnetic fields up to 56 T were generated with a 200 ms 3 MJ pulse with a 50 ms sinusoidal rise time and an exponential fall off. The use of pulsed magnetic fields limits the maximum exposure to very short times in order to have a well defined field value. In this experiment, 1 ms exposures were taken every 4 ms to collect data in $\sim$10 T steps.

3 Experimental Results and Discussion

3.1 Field-Induced Band Gap Shrinkage

Figure 3(a) shows the predicted field-periodic band structure for the case of a chiral SWNT. Here the band gap (normalized to the zero-field value) is plotted as a function of applied magnetic flux (normalized to ϕ_0). Both K and K' states are included, which results in a rather complicated behavior, but the lowest energy (i.e., band gap) is indicated as the thick solid line. In the field range used in this work, the value of ϕ/ϕ_0 does not exceed 0.01, and so we expect a monotonic

decrease of band gap as we increase the field. This is indeed what we observed. Figure 3(b) shows low-temperature (5.5 K) PL spectra at zero field and 55 T. Each PL peak, whose energy is a measure of the separation between the conduction and valence bands, shifts to a lower energy, indicating that the band gap shrinks with B.

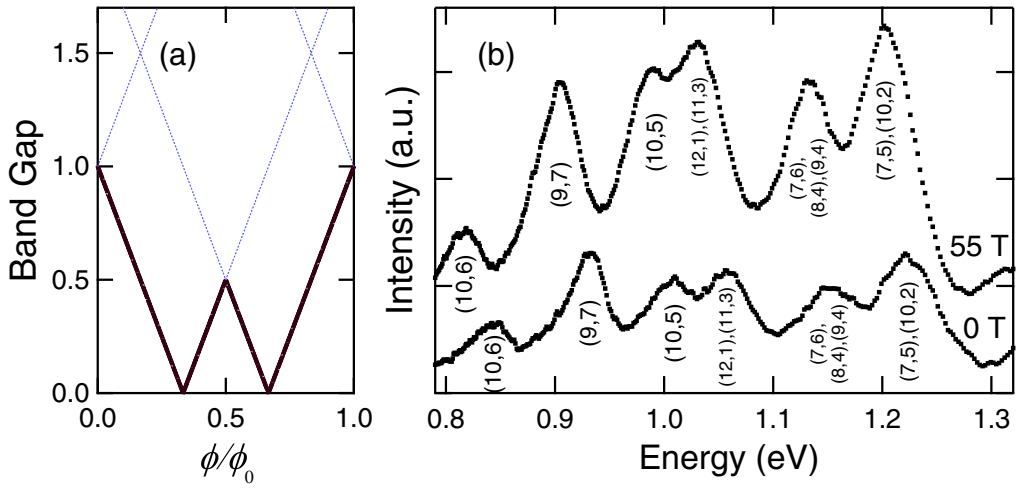

Fig. 3 (a) Aharonov-Bohm oscillation of band gap in a semiconducting SWNT [17]. Band gap, normalized to the zero-field value, is plotted versus magnetic flux, normalized to the magnetic flux quantum. (b) PL spectra at 5.5 K taken at 0 T and 55 T with an excitation wavelength of 780 nm. Each peak, assigned to a particular chirality (n, m), shifts to a lower energy with magnetic field due to field-induced band gap shrinkage, as expected from (a). The two traces are vertically offset for clarity.

3.2 Magnetic Brightening

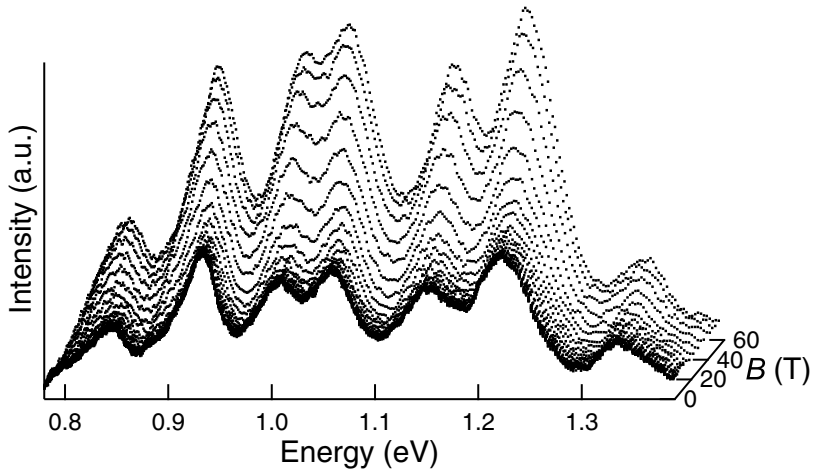

Fig. 4 The magnetic field evolution of the low-temperature PL spectrum up to 55 T for a stretch aligned SWNT-gel film, demonstrating magnetic brightening.

We found that a magnetic field significantly increases the PL intensity, especially at low temperatures. This 'magnetic brightening' behavior can be understood with a model qualitatively described in Section 1. Detailed and quantitative comparisons between experiment and theory are in progress and will be discussed elsewhere.

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