Excitons in Carbon Nanotubes with Broken Time-Reversal Symmetry

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Near-infrared magneto-optical spectroscopy of single-walled carbon nanotubes reveals two absorption peaks with an equal strength at high magnetic fields (>55 T). We show that the peak separation is determined by the Aharonov-Bohm phase due to the tube-threading magnetic flux, which breaks the time-reversal symmetry and lifts the valley degeneracy. This field-induced symmetry breaking thus overcomes the Coulomb-induced intervalley mixing which is predicted to make the lowest exciton state optically inactive (or dark).

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A striking prediction for single-walled carbon nanotubes (SWNTs) in a magnetic field (B) parallel to the tube axis is that the band gap oscillates with period ϕ_0, the magnetic flux quantum [1]. This is due to the appearance of the Aharonov-Bohm (AB) phase, $2\pi\phi/\phi_0$ (where ϕ is the tube-threading flux), in the circumferential boundary condition on the electronic wave function. As a result, metallic tubes become semiconducting even in an infinitesimally small B and semiconducting tubes can become metallic in ultrahigh B. Furthermore, the degeneracy between "left-handed" and "right-handed" electrons having Bloch vectors with opposite helicity (or the K and K' points in graphene k space) can be lifted by a B, which is expected to appear as AB-phase-dependent spectral peak splittings and shifts in interband optical spectra [2–5]. While low-temperature magnetotransport experiments are strongly affected by disorder and quantum interference effects [6], magneto-optical studies should be able to provide more clear-cut evidence of these predictions, with quantitative information on the splitting rates with B.

Optical processes are strongly affected by Coulomb interactions, especially in low-dimensional systems such as carbon nanotubes. Interband optical transition energies can be significantly different from predictions based on simple band structure models due to quasiparticle corrections and excitonic shifts, both of which have been shown to be extremely large in SWNTs [7–9]. There is growing experimental evidence [10,11] that absorption and photoluminescence (PL) peaks are excitonic in character, which is supported by recent theoretical studies [12–17]. One important and unresolved issue is whether optically inactive, or "dark," excitons exist. Such an exciton state is predicted to exist *below* the first optically active (or "bright") exciton state due to K-K' Coulomb mixing [15–17] and could explain experimentally observed low quantum efficiencies. A magnetic field can provide insight into this problem by lifting the K-K' degeneracy in a controllable manner, especially when it is sufficiently strong that the AB splitting exceeds the dark-bright energy separation. 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 bondinglike 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 [16]. The higher (lower) state is predicted to be bright (dark). When a symmetry-breaking perturbation (i.e., B) is applied, the K-K' degeneracy is lifted and the importance of the Coulomb mixing reduces. At high enough B where

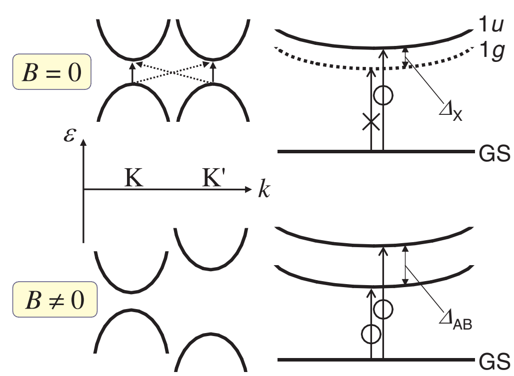

FIG. 1 (color online). The expected B evolution of K-K' intervalley mixing and splitting in a single-particle picture (left) and an excitonic picture (right). $1u$ ($1g$) is the bonding (antibonding) superposition state of the K and K' exciton states. The solid (dashed) line represents a bright (dark) exciton state. Δ_X: Coulomb-induced splitting; Δ_{AB}: Aharonov-Bohm-induced splitting. Both lowest (singlet) exciton states become bright at high enough magnetic fields such that $\Delta_{AB} > \Delta_X$. GS: ground state.

$\Delta_{AB} > \Delta_X$, both states become bright and two peaks with an equal intensity are expected.

Previous magneto-optical studies [18,19] using high dc magnetic fields up to 45 T revealed field-induced optical anisotropy and spectral changes in absorption and PL spectra. Quantitative analysis of the PL spectra showed agreement with existing theory [1,5]. However, the expected absorption splittings in the first-subband region were not resolved, presumably because the fields used were not large enough to make the splittings larger than the linewidths. In addition, no spectral changes were observed in the second-subband region, where linewidths are even larger.

Here we report on the first observation of clear absorption peak splittings. We performed interband absorption and PL experiments in micelle-suspended SWNTs in pulsed B up to 74 T. At fields above ~55 T, we observe clear splittings of absorption peaks associated with the lowest-energy interband transitions in semiconducting SWNTs in addition to the previously observed redshifts of PL peaks. The amounts of splittings and shifts as a function of B are successfully explained by our model taking into account the field-dependent band structure as well as the angular distribution of nanotubes. These results provide the first clear verification of the theoretical prediction that the K-K' degeneracy of the lowest states in semiconducting SWNTs can be lifted by a strong B along the tube axis via the AB phase, which produces two equally bright exciton states.

The samples consisted of SWNTs with diameters 0.6–1.3 nm suspended in sodium cholate and heavy water. They were prepared through homogenization, high power sonication, and centrifugation, similar to other processes using sodium dodecyl sulfate [20]. Such samples are rich in unbundled nanotubes surrounded by sodium cholate surfactant molecules, and are thus prevented from interacting with each other, and show chirality-dependent peaks in absorption and PL spectra [20,21]. Lowest-energy interband absorption peaks E_{11} (at 0.8–1.5 eV) are associated with the transitions between the highest valence subband and lowest conduction subband in semiconducting SWNTs with various chiralities while second-subband transitions E_{22} occur at 1.35–2.25 eV.

We performed magnetoabsorption and magneto-PL measurements in pulsed B fields up to 74 T at room temperature using a Si charge-coupled device (in the visible) and an InGaAs array detector (in the near infrared). All measurements were made in the Voigt geometry, i.e., the light propagation vector perpendicular to B. Spectra were recorded using a typical exposure plus readout time of ~1.5 ms. Measurements were performed in a variety of pulsed magnets. In Toulouse, magneto-optical absorption measurements were made using a 75 T magnet (the ARMS magnet [22]). At Los Alamos, both absorption and PL studies were performed in a capacitor driven 67 T magnet having a 10 ms rise time and an exponential decay. Absorption studies were also performed using a prototype insert coil for a planned 100 T multi-shot magnet [23]; operating independently, this insert magnet produced 75 T fields with a 5 ms rise time.

Figure 2(a) shows B-dependent absorption spectra in the E_{11} region up to 71.4 T. The light was linearly polarized along the B direction, i.e., $\hat{\varepsilon} \parallel \vec{B}$, where $\hat{\varepsilon}$ is a unit vector in the polarization direction. The absorption increases with B in this configuration due to the fact that the nanotubes align with B [18] and the E_{11} absorption occurs only for the light polarized parallel to the tube axis [2]. Three main peaks are dominant at zero B, and are labeled A, B, and C. Here, peak A (~0.88 eV) consists primarily of five types of SWNTs $[(n, m) = (9, 8)$, (10,6), (11,6), (12,2), and (11,4)], peak B (~0.98 eV) consists of five types [(10,3), (10,5), (8,7), (11,1), and (9,5)], and peak C (~1.1 eV) consists of four types [(7,6), (8,4), (9,2), and (9,4)]. At fields above ~55 T, each of these peaks splits into two clearly resolved peaks (e.g., peaks A^+ and A^-). Figure 2(b) shows 0 and 67 T absorption spectra (solid lines) for parallel and perpendicular polarizations together with theoretical curves (dashed lines) obtained through our model (described later). No traces are intentionally offset, and it is seen that absorption increases (decreases) with B for parallel (perpendicular) polarization, and the splittings are visible only in the parallel case.

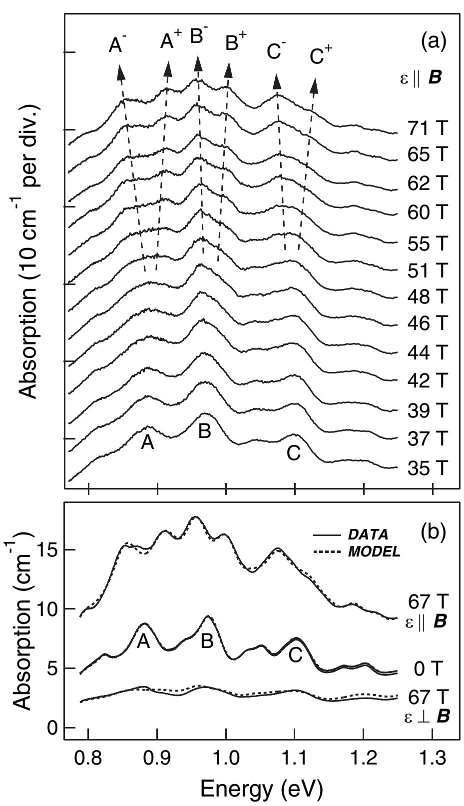

FIG. 2. Near band-edge absorption in semiconducting SWNTs in high magnetic fields for (a) polarization parallel to B (traces are offset) and (b) both polarizations (no intentional offset). Each of the three main peaks (labeled A, B, and C) splits into two at fields above ~55 T. Dotted lines in (b) are calculations based on the Aharonov-Bohm effect and magnetic alignment.

Figure 3 shows the B dependence of $\hat{\varepsilon} \parallel \vec{B}$ data (solid lines) and calculations (dashed lines) in the second-subband (E_{22}) region. Again, there are two main B-induced effects. First, absorption increases with increasing B due to magnetic alignment. Second, absorption peaks show broadening at high fields, but no clear splitting is observed even at the highest B. This is due to the much broader linewidths (~100 meV) of E_{22} transitions compared with E_{11} transitions (20–30 meV). The large linewidths of E_{22} transitions are consistent with short intraband relaxation times [24].

The B evolution of PL spectra up to 67 T taken with 792.5 nm excitation is shown in Fig. 4(a). The traces are vertically offset for clarity. Peaks are labeled by the corresponding dominant chiralities (n, m). Here a highly nonlinear B dependence is observed, i.e., drastic spectral changes occur only at high enough magnetic fields. At fields from 0 to 16 T, each peak slightly broadens with increasing B, but their peak positions remain the same. With further increasing B, however, all peaks start shifting to lower energies rather abruptly and continue to redshift with B up to the highest field (67 T). All the traces in Fig. 4(b) and the dotted lines in 4(a) are theoretical curves, which successfully simulate the corresponding experimental curves in Fig. 4(a). As detailed below, these simulations were obtained by taking into account the AB-effect-induced band structure modifications together with magnetic alignment.

For a nanotube in a parallel B, the amount of AB-induced K-K' splitting Δ_{AB} is expected to be proportional to B, i.e., $\Delta_{AB} \equiv \upsilon B$, when $\phi/\phi_0 \ll 1$. Here the rate of splitting υ is chirality dependent and, for a 1 nm-diameter nanotube, υ is expected to be $\sim$1 meV/T [1,5]. However, experimentally, we are measuring peak splittings and shifts for an *ensemble* of nanotubes with different angles (θ) with respect to the B direction. Using Maxwell-Boltzmann statistics under equilibrium conditions, the probability $P(\theta)d\theta$ of finding a nanotube in an angular range of $(\theta, \theta + d\theta)$ can be written in spherical coordinates as

$$P_u(\theta)d\theta = \frac{\exp(-u^2\sin^2\theta)\sin\theta d\theta}{\int_0^{\pi/2}\exp(-u^2\sin^2\theta)\sin\theta d\theta}, \quad (1)$$

$$u \equiv [B^2N(\chi_\parallel - \chi_\perp)/k_BT]^{1/2}, \quad (2)$$

where N is the number of moles of carbon atoms in the nanotube, and $\chi_\parallel$ and $\chi_\perp$ are parallel and perpendicular diamagnetic susceptibilities per mole of carbon atoms. Using this distribution function and Δ_{AB}, we modeled the PL data measured with two excitation wavelengths (792.5 and 750 nm) in the same way as in our previous work [18]. The 0 T spectrum was fitted using Lorentzians that represent the various chiralities present in the sample. We did not explicitly include intervalley Coulomb interaction in our model. The 67 T PL spectrum was then simulated by varying the two parameters u and υ for each Lorentzian with the linewidth determined at 0 T. For any given θ, υ was multiplied by $\cos\theta$ to account only for the tube-threading component of the magnetic flux. The relative intensities of the split peaks were calculated through the Boltzmann factor $\exp(-\Delta_{AB}\cos\theta/k_BT)$ with $T =$ 300 K, where k_B is the Boltzmann constant, while keeping the total integrated intensity equal to that of the zero-field peak. Averaging over θ was performed with a weight equal to $P_u(\theta)$. The average splitting rate obtained in this way was $\upsilon = 0.9$ meV/T. Data at intermediate fields ($0 < B <$ 67 T) were then simulated without any adjustable parameters, as shown in Fig. 4(b). Here, for each peak at each B, the value of u was calculated from the 67 T value through the u-B proportionality, i.e., Eq. (2), and there is good overall agreement with the data in Fig. 4(a). The obtained

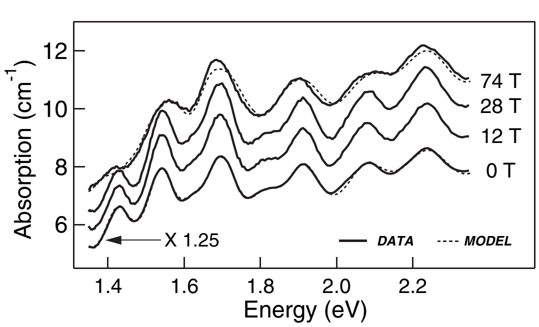

FIG. 3. Interband magnetoabsorption data (solid lines) and calculations (dashed lines) for light polarized parallel to B in the second-subband range. Data at nonzero B were taken during the falling slope of the B pulse. Each peak becomes broader with B.

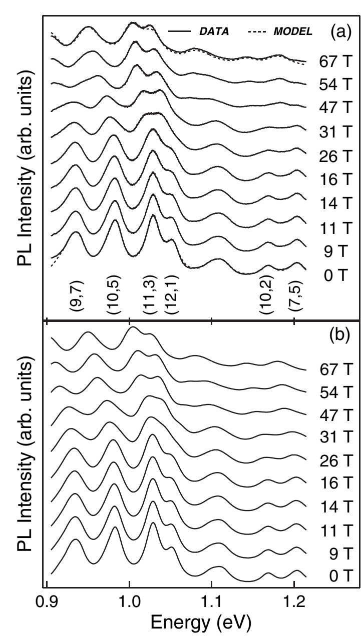

FIG. 4. (a) Photoluminescence spectra (solid lines) at various B with 792.5 nm excitation. Data at nonzero B were taken during the falling slope of the B pulse. The dashed lines are simulations. (b) Theoretical simulations of the magneto-PL data shown in (a).

v agrees with our low-B (<45 T) results [18], and the successful simulation of the PL data demonstrates that, although the nanotubes are not exactly under equilibrium conditions due to the use of pulsed B, Eq. (1) still adequately describes the angular distribution.

In PL, the relative intensities of the split peaks are affected by the population difference, and the higher energy peak becomes less and less visible as B (and thus Δ_{AB}) increases. Split *absorption* peaks, on the other hand, should have the same oscillator strength. To test this, we modeled the absorption data in essentially the same manner as for the PL data but *without a Boltzmann factor*. We took into account the effect of the polarizer used in the experiment through a factor of $\cos^2\alpha$, where α is the angle between the tube axis and the polarizer axis. The model works well for the 67 T absorption data in the $\hat{\varepsilon} \parallel \vec{B}$ case [see Fig. 2(b)] with $u_{avg} = 1.9$ and $v = 0.7$ meV/T [25]. Using the same values of u and v, the 67 T $\hat{\varepsilon} \perp \vec{B}$ absorption data were also reproduced successfully [see Fig. 2(b)]. The same model was then applied to the absorption in the second-subband region and, as shown in Fig. 3, the broadenings observed were well explained. These results confirm that there are two equally bright exciton states at high B (>55 T).

In summary, we have performed magneto-optical experiments on semiconducting SWNTs in pulsed magnetic fields up to 74 T. Clear splittings of absorption peaks in the first-subband region as well as significant redshifts of PL peaks were observed as a consequence of the Aharonov-Bohm phase changing the band structure. The observation of clear absorption peak splittings at high magnetic fields not only provides direct evidence of the expected K-K' splitting due to the B-induced symmetry breaking but also sheds some light on the issue of dark excitons. Recent theories predict that one of the lowest two excitons is dark. Our data demonstrate that both lowest-energy excitons are bright when a high enough magnetic field is applied along the tube axis. However, because splitting is only resolvable at high magnetic fields, these high-field studies do not allow quantitative determination of zero-field parameters particular to the dark exciton such as Δ_X.

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[25] The value for v deduced from 67 T absorption is smaller than that obtained from 67 T PL. This is most likely due to the chirality dependence of v. Absorption peaks are dominated by chiralities that are relatively abundant in the sample while PL probes only a limited number of chiralities (using only two excitation wavelengths in the current study). Thus, more PL data are needed to elucidate this point.