P H Y S I C A L   R E V I E W   L E T T E R S

Role of Bright and Dark Excitons in the Temperature-Dependent Photoluminescence of Carbon Nanotubes

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We report studies of the temperature dependence of the photoluminescence efficiency of single walled carbon nanotubes which demonstrate the role of bright and dark excitons. This is determined by the energy splitting of the excitons combined with 1-D excitonic properties. The splitting of the bright and dark singlet exciton states is found to be only a few meV and is very strongly diameter dependent for diameters in the range 0.8–1.2 nm. The luminescence intensities are also found to be strongly enhanced by magnetic fields at low temperatures due to mixing of the exciton states.

The optical properties of single walled carbon nanotubes (SWCNT) have been the subject of intense interest in recent years, since the discovery that separated SWCNT [1,2] exhibit well resolved fluorescence signals, making it possible to assign optical transitions to specific (n, m) semiconducting SWCNTs [3,4]. The role of excitons in both the transition energies, the quantum efficiencies, and the exciton lifetimes is now a matter of considerable debate. Experimental evidence suggests that exciton binding energies are of order several hundred meV [5–8] in agreement with first principles calculations [9,10] although there is also a substatial compensation of the excitonic interactions due to screening and electron-electron interactions [11,12]. The presence of two valleys, together with the electron and hole spins leads to multiple exciton states with only one, an odd parity spin singlet, predicted to be optically allowed (bright) [13]. The most strongly bound exciton is thought to be an optically forbidden (dark) triplet state [9,10,14–16] which could lead to very strong optical quenching. Experiment has shown [17] that the radiative lifetime in nanotubes is 3 to 4 orders of magnitude longer than the fluorescence decay times, suggesting that nonradiative processes are dominant. The singlet manifold is at higher energies [16,18,19] within which the lowest state is again dark, but with the bright exciton state quite close in energy. It has recently been predicted that the distribution of excitons between the different states will have a strong effect on the radiative lifetime of the excitons and how this depends on temperature [18,19], while preliminary experimental evidence suggests that for (6,4) nanotubes, a peak in radiative lifetime occurs in the region of 60 K [20]. In this Letter, we present a detailed study of the temperature dependence of the photoluminescence (PL) efficiency of SWCNT, which demonstrates the role of the excitons at different temperatures and allows estimates to be made of the singlet dark-bright exciton energy splittings. We also find that a significant degree of mixing of the excitonic states occurs which can be increased by the application of a magnetic field.

Purified SWCNTs were purchased from Carbon Nanotechnologies which were synthesized by the HiPCO method and consist of tubes with a broad band gap distribution. The nanotubes were then dispersed in D_2O solutions with sodium dodecylbenzene sulphate (SDBS) surfactants, prepared by sonication and ultracentrifuge following the method suggested by O'Connell *et al.* [1]. Samples were prepared by quench freezing in liquid nitrogen prior to immersion in a continuous He flow cryostat within a 20 T superconducting magnet.

PL and photoluminescence excitation (PLE) maps were studied using excitation with a conventional Ti:sapphire laser, an InGaAs array detector, and a 0.3 m grating spectrometer. In order to ensure accurate determination of the PL intensities from each tube species, PLE maps of the dominant species [4] were measured for each different temperature to ensure that each species was always measured under resonant excitation conditions. This allows us to take account of the shifts in the band gap energies caused by strain and temperature [21–26], although most of these changes take place at higher temperatures than those where the intensity is found to change most strongly. A typical PLE map is shown as the inset to Fig. 1. The intensities of the PL emission were analyzed for each peak at a series of temperatures from 1.5 to 250 K as shown in Fig. 1. All the nanotube PL intensities show a similar behavior with the intensity increasing progressively as the temperature falls until it reaches a maximum in the region of 10–40 K and then falls rapidly at lower temperatures. We interpret this behavior as being dominated by the temperature dependence of the radiative decay rate. Calculations of the decay rate have recently been reported by Spataru *et al.* [18] and Perebeinos *et al.* [19] in which it has been shown that the decay is dominated by two factors (i) for a single 1D exciton with a parabolic dispersion, the radiative lifetime is known to vary as $\tau_r \propto T^{1/2}$ [27] and (ii) the thermal distribution of the excitons between the different bright and dark exciton states. The initial optical excitation creates excitons in the optically active states which are spin singlets with odd parity. In principle, scattering into even
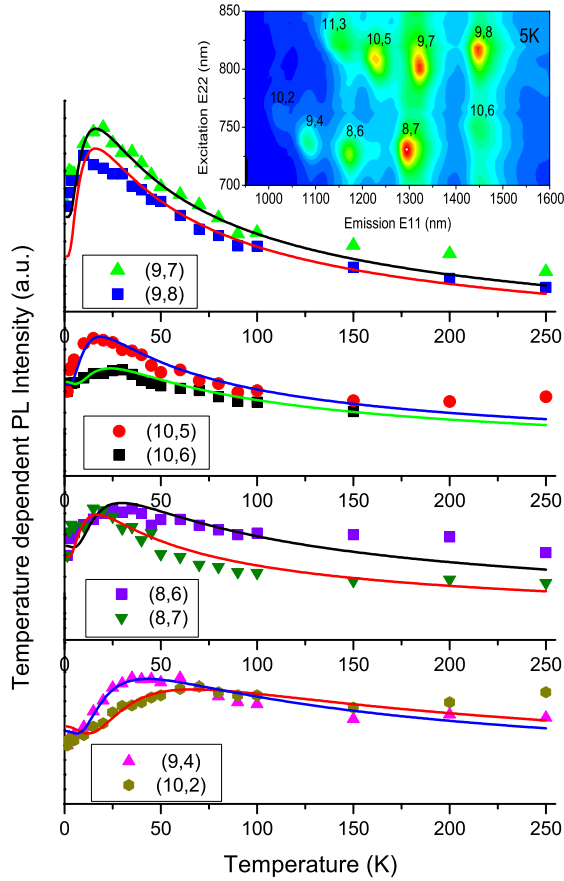
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FIG. 1 (color online). Temperature dependence of the PL intensities deduced for specific nanotube species. The inset shows a typical PLE map measured at 5 K.

parity and triplet states is forbidden except for some symmetry breaking processes which are weak [18,19]. Thermalization due to both parity breaking and spin-flip scattering were considered separately by Perebeinos *et al.* [19], while Spataru *et al.* [18] ignore spin-flip scattering. The origin of the scattering, or mixing of the states, is not certain but is likely to originate from effects such as disorder, defects, environmental coupling, or impurities.

We model the temperature dependence of the intensity (*I*) seen in Fig. 1 with the relation

$$I \propto \frac{1}{(T^2 + T_0^2)^{1/4}} \frac{m + e^{-\Delta/kT}}{1 + e^{-\Delta/kT}} \tag{1}$$

which is based on the simplification that recombination is dominated by radiative emission from two 1-D parabolic excitons, one dark and at a lower energy and one bright, corresponding to the two lowest energy singlet states. The energy separation is Δ, and we assume that there is a finite mixing of the spectral weight between the even and odd parity states of magnitude m, which is equal to the relative probability of radiative emission from the nominally "dark" state [16,28] relative to the "bright" state. This uses the same assumptions as in Spataru *et al.* [18], that

thermalization occurs only within the singlet states. The $T^{-1/2}$ divergence at low temperatures is removed by the addition of a small Lorenzian broadening term of $T_0 = 1$ meV which is comparable to the broadening observed in measurements on individual nanotubes [29]. Figure 1 shows fits to Eq. (1) for the 8 strongest nanotube species observed. The parameters deduced from the fitting are shown in Table I. The values deduced for Δ are quite strongly constrained by the temperature position of the maximum in intensity although the interaction of the values of the energy splitting and the mixing parameter m lead to fitting errors in the order of $\pm 15\%$ for Δ and $\pm 40\%$ for m, depending on the significance attached to the higher temperature data. Systematic effects, such as the influence of nonparabolicity in the exciton dispersion [19], the assumption that the emission is dominated by radiative terms within the singlet manifold, and possible temperature-dependent strain effects [21,22] are more likely to become significant above 100 K and may also lead to some errors, particularly in the values deduced for m which are more dependent on the high temperature behavior.

The energy separation Δ is found to be relatively small which is thought to be consistent with the assumption that emission is dominated by the spin singlet manifold of exciton states. The values are comparable to the values calculated by Perebeinos *et al.* [19] at a diameter d of ~ 1 nm, but are considerably smaller than has been suggested by some authors [5,18,28]. The splittings are also considerably smaller than the typical nanotube linewidth (full width of order 20 meV) which explains why the two exciton states cannot be resolved in an ensemble measurement as reported here. The fitting also suggests that there is a considerable degree of spectral mixing between the even and odd parity states (on the order of 0.2) which increases as the tube diameter becomes smaller.

Figure 2 shows the values of Δ and m as a function of the nanotube diameter (d). The splitting between the bright and dark singlet exciton states shows a very clear and

TABLE I. Fitting parameters deduced from the temperature dependence of the PL intensities studied at both 0 and 19.5 T.

n	m	Diameter[a] (nm)	Δ (meV)	m	Δ(19.5 T) (meV)	m(19.5 T)
8	3	0.78	5.3[a]	0.07[a]		
7	5	0.83	4.6[a]	0.08[a]		
10	2	0.88	5.5	0.11		
9	4	0.92	3.4	0.14	3.4	0.39
8	6	0.97	2.6	0.18	2.6	0.41
12	1	0.99	1.9	0.19		
11	3	1.01	1.9	0.19		
8	7	1.03	1.3	0.25	1.3	0.3
10	5	1.05	1.5	0.23	1.5	0.64
9	7	1.10	1.2	0.25	1.2	0.52
10	6	1.11	2.6	0.27		
9	8	1.17	1.0	0.2	1.0	0.38

[a]Data for the two lowest diameter tubes were deduced using 633 nm excitation only, which is close to resonance in the temperature range 1.6–100 K.
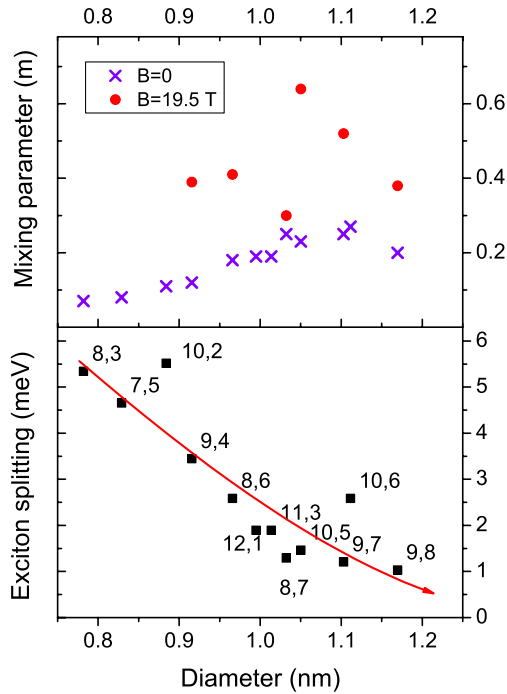
FIG. 2 (color online). Values deduced for the energy gap between the lowest singlet dark exciton state and the bright, optically allowed state, together with values for the mixing parameter of the dark and light excitons, as a function of nanotube diameter.

strong dependence on the tube diameter, decreasing from ~5 meV at 0.8 nm down to ~1 meV by 1.1 nm which is much more rapid than the predicted scaling with excitonic size $\propto 1/d$ [9,15,19]. This behavior is consistent with the recently reported calculations from Ando [13], which predict that the relative energies of the bright and dark exciton states are strongly dependent on the Coulomb interaction strength, which is parameterized in terms of a factor w_1/w_2 which is related to the relative contribution to short range electron-electron interactions from intra and intervalley processes. For a diameter of ~1.4 nm, it is predicted that the bright singlet exciton crosses the first dark singlet state at about $w_1/w_2 = 0.25$ which is consistent with our very small value of Δ at 1.3 nm. The increase in Δ that we measure as d decreases suggests that w_1/w_2 rises to ≈ 0.28 by 0.8 nm. The mixing parameter also shows a clear increase in magnitude with tube diameter, but has significantly greater error from the analysis.

The transition to a simple $T^{-1/2}$ behavior above 100 K shown in Fig. 1 suggests that optically pumped radiative emission from nanotubes can be described in terms of emission dominated by the optically active (bright) excitons for high temperatures. This leads to the conclusion that scattering into the triplet spin states is in fact very weak, and the optical properties of the nanotubes will be dominated at room temperature by the optically active exciton states. There is still strong evidence in the literature for high nonradiative recombination rates [17,20]; how-

ever, our data suggests that this is not related to the splitting into bright and dark exciton states. The magnitudes deduced for the mixing terms are also quite significant (of order 10–20%) which leads to the relatively high level of emission at low temperatures. This may well be related to the relatively high degree of strain in the nanotubes which is caused by the freezing process [21].

In order to investigate the role of the mixing terms, we also investigated the influence of a magnetic field, which it has been suggested could lead to enhanced mixing of the singlet excitonic levels. This results from the lifting of the degeneracy of the K and K' states [30] which control the symmetry of the excitons [13,28,31] by the addition of an Aharanov-Bohm phase to the nanotube. Measurements at room temperature have observed this splitting at very high fields [31,32], but see no significant increases in overall intensity [31]. Single wavelength excitation measurements [33] have, however, shown strong PL enhancement at low temperatures. The PLE experiments were therefore repeated at a magnetic field of 19.5 T with PLE maps again being measured at each temperature. The experiments were performed in the Voigt geometry with the excitation and emission polarized parallel to the magnetic field, which will strongly select tubes which are oriented parallel to the magnetic field. Typical results are shown in Fig. 3 which demonstrates two characteristic features. First, at low temperature, the magnetic field causes a very significant increase of the PL intensity. Second, at high temperatures, a small reduction in intensity is observed, which is associated with a broadening of the PL emission due to the appearance of the (unresolved) Ajiki-Ando splitting [30–32]. The temperature dependence was refitted using Eq. (1) as shown for two species in Fig. 3.
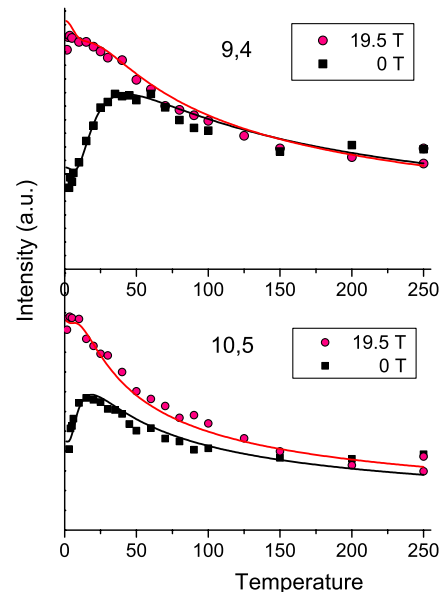

FIG. 3 (color online). Temperature-dependent PL intensities for selected nanotube species at zero and 19.5 T, showing experiment and fits using Eq. (1).
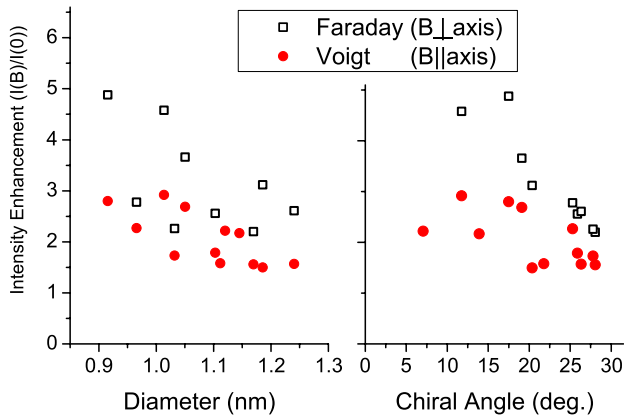
FIG. 4 (color online). The magnetic field induced intensity
enhancement $I(B)/I(0)$ produced by a magnetic field of 19.5 T

The effect of the magnetic field could be modeled sim-
ply by changing the magnitude of the mixing parameter,
which had the immediate effect of increasing the emission
at low temperatures, where the dominant emission pro-
cesses are from the nominally dark exciton. This behavior
is in excellent agreement with the results of Ando [13],
which predict a rapid rise in intensity for the lower energy
state caused by the field induced mixing of the wave
functions. The increases in m are plotted in Fig. 2 and
show that the mixing increases up to values of order 50%
as predicted by Ando [13], who has calculated that a field of
20 T ($\phi/\phi_0 = 0.005$) is sufficient to induce an intensity
ratio of 2:1 for the two singlet states. In some cases, slight
improvement to the fits could be achieved by assuming that
the magnetic field also caused a decrease in the splitting Δ,
although any such change was at the limit of the resolution
of the data.

The tube species with larger values of the exciton split-
tings and smaller values of d were more affected by the
magnetic field, as shown by Fig. 4 which plots the enhance-
ment in PL intensity $I(B)/I(0)$ produced by 19.5 T. The
enhancement becomes larger as the nanotube diameter
decreases, although the correlation is not as clear as for
the exciton splitting. The same data are also plotted as a
function of the nanotube chiral angle, which shows rather
more correlation. Much more surprisingly, however, when
the experiments were repeated using the Faraday geometry
(also shown in Fig. 4), it was found that the enhancement of
the PL intensities was even greater. In this case, the field is
perpendicular to the nanotube axes, where the arguments
for the simple Aharanov-Bohm phase mixing of the exci-
tonic states [30] no longer hold, suggesting that some other
mechanism may also be significant.

In conclusion therefore, we have shown that the tem-
perature dependence of the PL intensity from carbon nano-
tubes can be well described by a combination of a 1-D
excitonic behavior together with a small splitting between
bright and dark singlet exciton states which are quite
strongly and easily mixed. The splitting between the levels
is significantly smaller than has been predicted by some

theories and is strongly diameter dependent. The mixing
between the states can be significantly enhanced by the
application of a magnetic field which is shown to produce
significant increases in PL intensity at low temperatures.

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