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Spin-Related Novel Optical Phenomena in Single-Walled Carbon Nanotubes

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1. Introduction

The interplay between conduction electrons and localized spins is one of fundamental and important problems in modern condensed matter physics and gives us unexpected phenomena: It is well known that they induce resistivity minimum phenomena, known as the Kondo effect. Besides the conducting electrons, the fundamental question arises whether the interplay between photo-excited electrons and localized spins leads novel phenomena.

In this regard, semiconducting single-walled carbon nanotubes (CNTs) provide us an interesting research field of spin-related optical phenomena. Because of their quasi-one-dimensional structure, photo-excited electrons and holes in CNTs are strongly correlated each other and form a bound electron-hole pair, called an exciton. Owing to their large binding energy, the exciton in CNT exhibits remarkable stability up to room temperatures. Therefore, when there are localized spins in CNTs, optical phenomena are expected to exhibit wide variety cased by the interplay between exciton and the spins.

In this paper, we demonstrate two interesting examples of novel optical properties of CNTs that are induced by localized spins based on the theoretical investigations.

2. Defects Influences on Optical Properties of CNTs

Recent experiments have shown the evidence in which the excitons correlate with localized spin induced by the defects in CNTs. Such localized spin is essential in the bipartite lattice systems as is the CNTs [1,2,3]. However, unfortunately, the fundamental theory for this problem has not been addressed yet. We thus propose a theory that expresses the interaction between excitons and localized spins in CNT system. The interaction between excitons and localized spins induced by defects can be written as the exchange Hamiltonian expressed in terms of the spin operators for conduction and valence electrons and for the localized non-bonding states:

$$H = -(J_c \vec{s}_c - J_v \vec{s}_v)\cdot \vec{S}. \qquad (1)$$

Solving the Bethe-Salpeter equation by treating this term as a perturbation, we obtain the mixing states between the spin singlet and triplet excitons. From these states, we can calculate absorption spectra. Figure 1 shows the calculated absorption spectrum for (20,0) CNTs for J_c-J_v=5 meV, *S=1/2*, and a defect concentration of *5%*. This spectrum clearly shows the triplet exciton peak in addition to the singlet main peak. An optical transition between the ground and triplet states becomes possible through the singlet state in the perturbed triplet state. The satellite peak is asymmetric because triplet excitons with finite momenta that exceed the bottom of the energy band are excited.

From the calculation result, we can conclude that our theory clarifies the role of localized spins associated with defects on optical properties of CNTs.

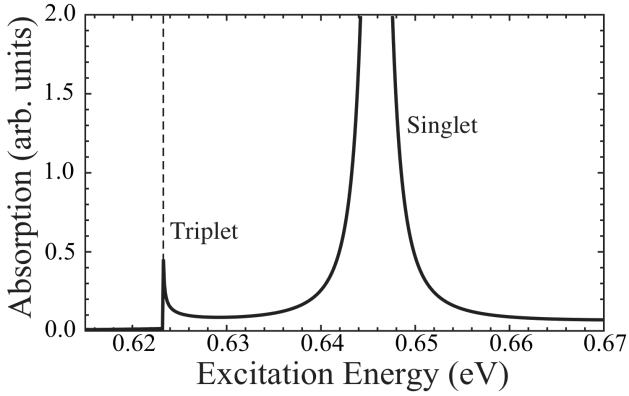

Fig.1 Absorption spectrum of (20,0) CNTs with defects.

3. Optical Properties of Ultrathin Magnetic Nanowires Encapsulated in CNTs

It has been pointed out that ultrathin magnetic nanowires encapsulated in carbon nanotubes are potential candidates for constituent elements in the next-generation spintronics and electronics devices [4]. For the device application, the probing methods for the magnetic state of the nanowires are essential and important. For such methods, we theoretically propose a non-contacted optical probing method based on the optical response from such magnetic nanomaterials encapsulated in carbon nanotubes. To discuss the effects of magnetic elements on excitons in nanotubes, we solve the Bethe-Salpeter equation that includes the exchange interaction between excitons and a ferromagnet. When the spins of ferromagnetic atoms are ferromagnetically ordered below the phase transition temperature, the polarized spins behave as an effective magnetic field to excitons:

$$H = g\mu s_z^{\ c} H_z^{\ c} - g\mu s_z^{\ v} H_z^{\ v}, \qquad (2)$$

where the effective field $H_z^{c(v)}$ is defined as $H_z^{c(v)}=-J_{c(v)}M/(g\mu)^2$, where μ is the Bohr magneton, $g=2$ is the g-factor, and M is the magnetization. The explicit form of the exchange integrals $J_c(J_v)$ in Eq. (2) depends on the materials being considered.

Equation (2) indicates that an electron in the conduction band and a hole in the valence band have different Zeeman energies due to the different exchange integrals. Accordingly, the spin degeneracy is broken in the presence of the exchange so that singlet and triple excitons can mix. After solving the Bethe-Salpeter equation including the Zeeman term represented by Eq. (2), we obtain the absorption spectra (Fig.2).

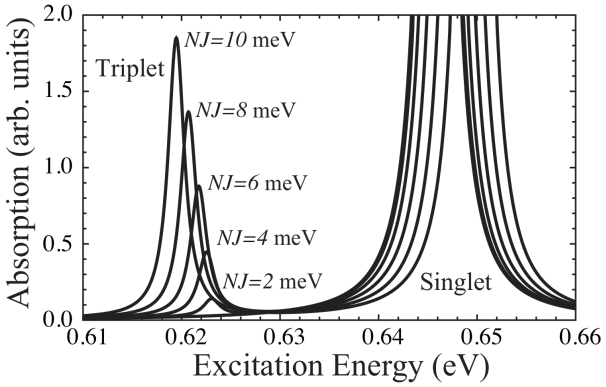

Fig.2 Absorption Spectra for the magnetic nanowire encapsulated in (20,0) CNTs.

The spectra in Fig. 2 are clearly sensitive to the ferromagnet. For finite values of $NJ(=NJ_c\text{-}NJ_v)$, a new peak appears in addition to the singlet exciton peak. The energy of the new peak is about 30 meV lower than that of the singlet peak, which indicates that the peak is associated with adsorption of a triplet exciton. The new peak is due to the triplet exciton acquiring finite oscillator strength. The peak intensity increases monotonically with increasing number of magnetic elements N and increasing exchange interaction J.

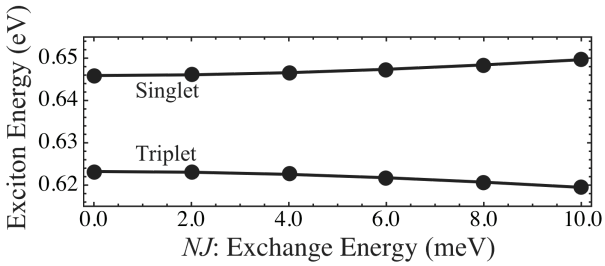

Fig.3 Exciton energies as a function of the exchange energy. The upper (lower) series is for a spin-singlet (triplet) exciton.

Furthermore, both the singlet and triplet peaks shift with increasing NJ. Figure 3 shows the exciton energies as a function of the exchange energy, NJ. With increasing exchange energy, the singlet (triplet) exciton is red (blue)-shifted due to mixing of the singlet and triplet excitons.

It is important to discuss the mechanism of the finite oscillator strength of the triplet excitons. Spin degeneracy is not broken without Zeeman coupling expressed by Eq. (2), which is associated with the exchange interaction between excitons and polarized spins in a ferromagnet. Therefore, without Zeeman coupling, the exciton spin states are classified according to whether they are singlet or triplet spin states and they produce the singlet peak in the absorption spectra. However, in the presence of Zeeman coupling (2), the exciton spin states cannot be classified according to whether they are the singlet and triplet spin states, which implies that singlet and triplet excitons mix with each other. Of the three degenerate triplet states, singlet excitons can couple only with a triplet exciton. The spin projection in the z-direction of the mixed triplet state is zero ($s_z = s_z^c - s_z^v = 0$). Singlet and triplet mixing occurs only if the exchange integrals for electrons and holes are different. The actual values of the exchange integrals depend on the encapsulated material.

Our calculation indicates that the mechanism presented above certainly detects magnetic ordering of nano-materials encapsulated in carbon nanotubes.

4. Conclusions

We studied the spin-related optical properties both for the CNTs with defects and for CNTs encapsulating the magnetic nanowires. We demonstrated that (1) our theory provides a unified explanation for the microscopic mechanism for optical activation of triplet dark excitons in CNTs with imperfections and (2) a new peak originated from the triplet exciton appears as a result of the interaction between the ferromagnets and the excitons in the magnetic nanowire encapsulated in CNTs. The present studies open the possibility for the novel application of spin-related optical devices of CNTs.

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