



Line-profile Formula in the Carbon Nanotubes by Electron Spin Resonance

Jung-Il Park¹ and Haeng-Ki Lee^{2*}

¹Nano Application Laboratory, Department of Physics, Kyungpook National University, Daegu 702-701, Korea

²Department of Radiotechnology, Suseong College, Daegu 706-711, Korea

(Received December 29, 2011; Revised May 26, 2012; Accepted June 08, 2012)

Abstract : The line-width of carbon nanotubes (CNTs) was studied as a function of the temperature at a frequency of 9.49 GHz in the presence of external electromagnetic radiation. The relative frequency dependence of the absorption power is obtained with the projection operator technique (POT) proposed by Kawabata. The line-width increased as the temperature increased in the high-temperature region ($T > 200$ K). The scattering is little affected in the low-temperature region ($T < 200$ K) because there is no correlation between the resonance field and the Fermi-Dirac distribution function. Thus, the present technique is considered to be more convenient to explain the resonant system as in the case of other optical transition problems.

Keywords: ESR, CNTs, Projection operator, Line-profile, Line-widths,

INTRODUCTION

Electron spin resonance (ESR) spectroscopy has been used to assess the quality of carbon nanotube, CNT.¹ In ESR experiments, one applies a static magnetic field and measures the absorption power of electromagnetic radiation polarized perpendicular to the field direction. In the absence of SU(2) spin symmetry breaking terms in the system Hamiltonian, the absorption power is then simply

Department of Radiotechnology, Suseong College, 15, Dalgubeol daero-528gil, Suseong-gu, 706-711, Korea

Tel: +82.53.749.7104 Fax: +82.53.749.7103 email:leeki@sc.ac.kr

Journal of the Korean Magnetic Resonance Society 2012 June; 16(1): 11-21

<http://dx.doi.org/10.6564/JKMRS.2012.16.1.011>

a delta peak at the Zeeman energy. Since spin-orbit coupling (SOC) are generally the leading terms breaking the SU(2) invariance, deviations in the absorption power from delta peak, e.g., shifts or broadenings, are directly connected to these coupling. Initially, it was assumed that a SOC in CNTs, due to p_z electrons, would lead to a long spin relaxation compared with typical semiconductors. However, numerous experimental measurements of spin transport and ESR in CNTs present some different results for the magnitude of the spin relaxation.^{2,3}

From a theoretical point of view, the studies performed thus far on a resonant system in the presence of electromagnetic radiation have usually been based on the following methodologies: Green's function approach, Feynmann's path integral approach, the Wigner representation approach, and the projection operator technique (POT). There have been numerous methods for the calculation of resonance line-widths. Among the above mentioned methods, we focus on the POT of Kawabata.⁴ By using this method, we succeeded in formulating a response theory,⁵⁻⁸ which includes the Kubo⁹ formalism as the lowest-order approximation.

In the present work, we calculate the line-width with the same proposition that Kawabata used and compare experimental data of Salvetat et al.¹⁰ Through numerical calculations, we analyze the relative frequency dependence of the absorption power and the temperature dependence of the line-width at a frequency of 9.49 GHz in the presence of external radiation. Finally, we discuss the results and draw conclusions.

SYSTEM

We begin with a few essential definitions concerning CNTs. The CNT is conveniently imagined as a spiral graphite sheet (graphene) rolled along the chiral vector \vec{C}_h as below (see Fig. 1)¹¹

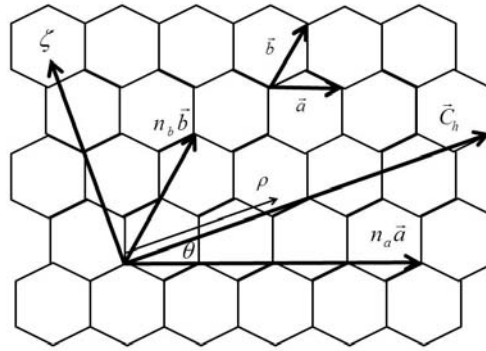


Figure 1. The lattice structure of graphene.

$$\vec{C}_h = n_a \vec{a} + n_b \vec{b}, \quad (1)$$

where $\vec{a} = a_{cc}(1, 0)$ and $\vec{b} = a_{cc}(1/2, \sqrt{3}/2)$ are the graphene lattice unit vectors with $a_{cc} = 0.246$ nm and n_a and n_b are integers, which characterize the geometry of a particular CNT.

The slop of \vec{C}_h is defined by

$$\theta = \tan^{-1} \left[\frac{\sqrt{3}n_b}{2n_a + n_b} \right], \quad (2)$$

and the diameter of the CNT is given by $|\bar{C}_h| = \sqrt{3}a_{cc}(n_a + n_b + n_a n_b)^{1/2}$, $d = |\bar{C}_h|/\pi$. The graphene two-valley band structure projects onto the CNT one so that in the vicinity of each valley the Hamiltonian takes the form:¹²

$$H_\lambda = H_z + \hbar v_F (\lambda \kappa_m \sigma_1 + k \sigma_2), \quad (3)$$

where the Fermi velocity is $v_F = 3 \times 10^5$ m/s, σ_1 and σ_2 are Pauli spin matrices and, k is the wave vector of electron. The energy band structure of graphene are located at the K and K' corner points of the first Brillouin zone. Which will be labeled by $\lambda = +1, -1$ respectively. In the reference frame (ξ, η, ζ) , the Zeeman Hamiltonian takes the form $H_z = \hbar \omega_z (\sin \alpha S_\xi + \cos \alpha S_\zeta)$, $\hbar \omega_z = g_e \mu_B B$ ($g_e = 2$ and μ_B is the Bohr magneton) so that the frequency of spin procession is given by

$$\omega_\lambda = \sqrt{(\omega_z \sin \alpha)^2 + [\omega_z \cos \alpha + 2\lambda(\Lambda_0 + \Lambda_1 \langle \sigma_1 \rangle) / \hbar]^2}. \quad (4)$$

$|\Phi_{k,+m,\lambda}^{CNT}\rangle$ is an eigenstates of H_λ for an spin-up electron; and $|\Phi_{k,-m,\lambda}^{CNT}\rangle$ for a down-spin electron. Then, $|\Phi_{k,\pm m,\lambda}^{CNT}\rangle$ satisfies the Schrödinger equation as below

$$H_\lambda |\Phi_{k,\pm m,\lambda}^{CNT}\rangle = \left(\pm \hbar v_F \sqrt{\kappa_{m,\lambda}^2 + k^2} + \hbar \omega_\lambda \right) |\Phi_{k,\pm m,\lambda}^{CNT}\rangle, \quad (5)$$

where $E_{\pm m} = \pm \hbar v_F \sqrt{\kappa_{m,\lambda}^2 + k^2} + \hbar \omega_\lambda$ is the CNT electronic spectrum. When a SOC is incorporated in the Hamiltonian H_λ , the SOC mediated by CNT curvature which take the simplest form in CNT coordinate as:

$$H_{so} = \Lambda_0 \lambda \sigma_0 2S_\zeta + \Lambda_1 \lambda \sigma_1 2S_\zeta - i\Lambda_2 \sigma_2 (S_+ e^{i\varphi} - S_- e^{-i\varphi}), \quad (6)$$

where σ_0 is identical matrix, $S_\pm = S_\zeta \pm iS_\eta$, $\varphi = 2\rho/d$, $0 < \rho < |\bar{C}_h|$. The electron spin operators $\sigma_\pm = \sigma_x \pm i\sigma_y$ are defined as $\sigma_+ = 2\sum_m a_{m+}^+ a_{m-}$, $\sigma_- = 2\sum_m a_{m-}^+ a_{m+}$. In Eq. (6), the SO constants are proportional to CNT curvature, $\Lambda_0 = (\delta_0/d) \cos 3\theta$, $\Lambda_{1,2} = \delta_{1,2}/d$, $\delta_1 = -0.19 \text{ meV}\cdot\text{nm}$, $\delta_0/\delta_1 = 4.5$, $\delta_2/\delta_1 = -1.4$, $\alpha = \pi/2$. We take into account that $\langle k, m, \lambda | \sigma_0 | k, m, \lambda \rangle = 1$, $\langle k, m, \lambda | \sigma_2 e^{\pm i\varphi} | k, m, \lambda \rangle = 0$, and $\langle k, m, \lambda | \sigma_1 | k, m, \lambda \rangle = \pm \lambda \kappa_{m,\lambda} / \sqrt{k^2 + \kappa_m^2}$. Here $+$ ($-$) corresponds to conduction (valence) band.

PROJECTION OPERATOR TECHNIQUE

When a polarized electromagnetic radiation with angular frequency ω is applied along the z -axis, the absorption power $P_{abs}(\omega)$ delivered to the system is given by

$$P_{abs}(\omega) = (H_0^2/2) \text{Re}[\chi_{+-}(\omega)], \quad (7)$$

here “Re” means “the real part of” and the electron spin susceptibility (ESS) $\chi_{+-}(\omega)$ is given, in the Kubo formalism, as

$$\chi_{+-}(\omega) = \frac{1 - e^{-\beta\hbar\omega}}{\omega} \sum_{\pm m} f(E_{\pm m}) [1 - f(E_{\pm m} + \hbar\omega)]$$

$$\times \langle k, +m, \lambda | \sigma_- | k, -m, \lambda \rangle \langle k, -m, \lambda | \sigma_- | k, +m, \lambda \rangle \langle \Xi_{+-}^{epr}(\omega) \rangle, \quad (8)$$

where $f(E_{\pm m})$ is the Fermi-Dirac distribution function for the electron state $|\Phi_{k, \pm m, \lambda}^{CNT}\rangle$. It is

convenient to write the expression of $\langle k, +m, \lambda | \sigma_+(t) | k, -m, \lambda \rangle$ in the second quantization

formalism as $\langle k, +m, \lambda | \sigma_+(t) | k, -m, \lambda \rangle = Tr^{(e)} \{ a_{-m}^+ a_{+m} \sigma_+(t) \}$, where $\sigma_+(t)$ on the right hand side

is a second quantized operator. Following Kawabata,⁴ we define two projection operators P_{+-} and

Q_{+-} as

$$P_{+-} Y \equiv \frac{(X_{+m-m}, Y)}{(X_{+m-m}, \sigma_+)} \sigma_+, \quad Q_{+-} Y \equiv \frac{(Y, \sigma_+)}{(X_{+m-m}, \sigma_+)} X_{+m-m}, \quad (9)$$

with $X_{+m-m} = a_{-m}^+ a_{+m}$. We easily see that P_{+-} and Q_{+-} satisfy the condition imposed on

projection operators, $P_{+-}^2 = P_{+-}$, $Q_{+-}^2 = Q_{+-}$ and

$(Q_{+-} X, (1 - P_{+-}) Y) = ((1 - P_{+-}) X, P_{+-} Y) = 0$. We consider the equation of motion as below

$$\Xi_{+-}(t) \equiv \frac{(X_{+m-m}, \sigma_+(t))}{(X_{+m-m}, \sigma_+)}. \quad (10)$$

We separate \tilde{X}_{+m-m} into two parts, parallel and orthogonal to \tilde{X}_{+m-m} . Then we obtain from

Eq. (10)

$$\begin{aligned} \frac{d\Xi_{+-}(t)}{dt} &= -\frac{(\exp(-iLt)\tilde{X}_{+m-m}, \sigma_+)}{(X_{+m-m}, \sigma_+)} = i\omega_0 \Xi_{+-}(t) - \frac{((1 - K_{+m-m})X_{+m-m}, \sigma_+(t))}{(X_{+m-m}, \sigma_+)}, \\ i\omega_0 &= -\frac{(\tilde{X}_{+m-m}, \sigma_+)}{(X_{+m-m}, \sigma_+)} = \frac{(X_{+m-m}, \tilde{\sigma}_+)}{(X_{+m-m}, \sigma_+)}, \end{aligned} \quad (11)$$

where $\tilde{X}_{+m-m} = iLX_{+m-m}$ and $K_{+m-m} = (1 - Q_{+-})X_{+m-m}$.

Next we separate $\sigma_+(t)$ into two parts, parallel and orthogonal to σ_+ , and using the useful relations $L_f\sigma_+ = \omega_0\sigma_+$, $Q_{+-}L_f\sigma_+ = 0$, $(L_fQ_{+-}X)_{+m-m} = 0$, since $P_{+-}\sigma_+ = \sigma_+$, from Eq. (11) it follows that K_{+m-m} and σ_+ are orthogonal to each other, i.e., $(Q_{+-}, \sigma_+) = 0$. Then we obtain

$$\frac{d\Xi_{+-}^{epr}(t)}{dt} = i\omega_0\Xi_{+-}^{epr}(t) - \int_0^t d\omega \Xi_{+-}^{epr}(\omega)\Gamma_{+-}^{epr}(t-\omega), \quad (12)$$

where $\Gamma_{+-}^{epr}(t) = (K_{+m-m}, R_{+m-m}(t)) / (X_{+m-m}, \sigma_+)$. We obtain the ESS as below

$$\chi_{+-}(\omega) = \sum_{\pm m} \frac{f(E_{+m}) - f(E_{-m})}{E_{+m} - E_{-m}} \frac{|(\sigma_+)_{+m-m}|^2}{i\hbar(\omega - \omega_0) - i\Gamma_{+-}^{epr}(\omega)}, \quad (13)$$

We see the coherent scattering factor Γ , call the line-profile formula, gives characteristics of the system because it is affected by the resonance mechanism. The lowest-order approximation of the line-profile is given as follows:

$$\begin{aligned} \Gamma_{+-}^{epr}(\omega) = & \sum_{\nu \neq \mu} \sum_{\Delta m \neq \pm 1} \frac{1}{(\sigma_+)_{+m-m}} \left\{ (1 + f(E_{\pm m})) \left[\sum_{j=1}^2 \frac{(\sigma_+)_{-m+m} A_j}{\hbar\omega - \varepsilon j^+} - \sum_{j=3}^4 \frac{(\sigma_+)_{+m-m} A_j}{\hbar\omega - \varepsilon j^+} \right] \right. \\ & \left. + f(E_{\pm m}) \left[\sum_{j=1}^2 \frac{(\sigma_+)_{-m+m} A_j^*}{\hbar\omega - \varepsilon j^-} - \sum_{j=3}^4 \frac{(\sigma_+)_{+m-m} A_j^*}{\hbar\omega - \varepsilon j^-} \right] \right\}. \quad (14) \end{aligned}$$

Eq. (14) is similar to Sawaki's result,¹³ which is based on the Stark ladder representation.

However, our formula uses more terms for expressing the Fermi-Dirac distribution. We consider the term $\Gamma_{+-}^{epr}(\omega) \equiv iS_{+-}^{epr}(\omega) + W_{+-}^{epr}(\omega)$, where the line-shift spectra is $S_{+-}^{epr}(\omega) = \text{Im}[\Gamma_{+-}^{epr}(\omega)]$, and

the line-width is $W_{+-}^{epr}(\omega) = \text{Re}[\Gamma_{+-}^{epr}(\omega)]$. We apply this approximate formula to the real system

for demonstration, we obtain absorption power as:

$$P_{abs}(\omega - \omega_0) \propto \frac{1}{\omega_z} \int_{-\infty}^{+\infty} dE_{\pm m} \frac{W_{+-}^{epr}(\omega) [f(E_{-m}) - f(E_{+m})]}{[\omega - \omega_0 - S_{+-}^{epr}(\omega)]^2 + [W_{+-}^{epr}(\omega)]^2}, \quad (15)$$

The absorption power is described by the Lorentzian form. Fig. 2 shows the relative frequency dependence of the absorption power, for the spectrum of the CNT at 150, 200, 250, and 300 K. From the absorption power, we can see the broadening effect near the resonance peak, which exhibits increase as the temperature increases. In Fig. 3, the temperature dependence of line-width compare with experimental data of Salvetat et al.¹⁰

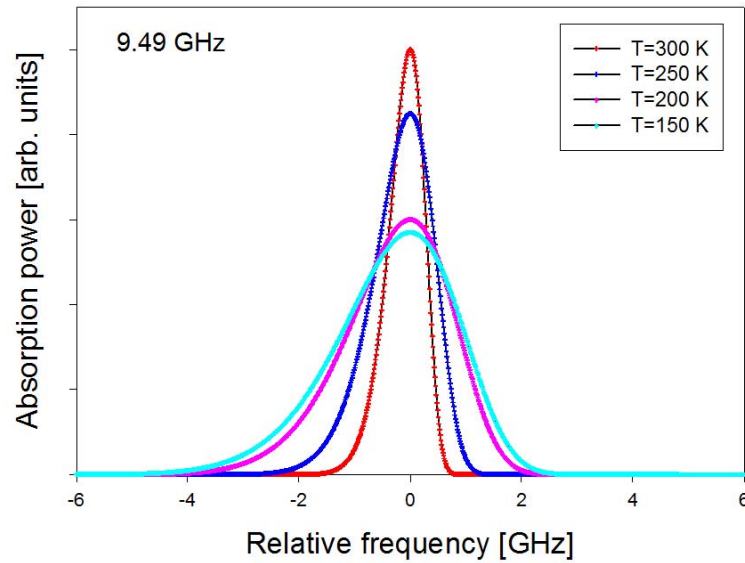


Figure 2. The Relative frequency dependence of the absorption power $P_{abs}(\omega - \omega_0)$ curves of EPR at 150, 200, 250, and 300 K in the CNT at a frequency of 9.49 GHz.

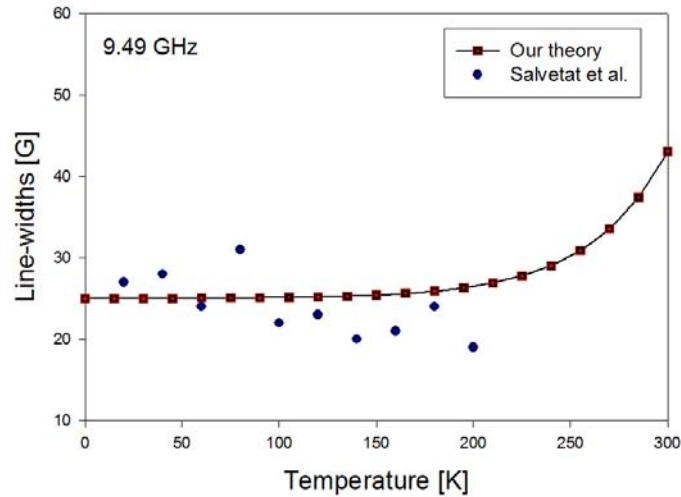


Figure 3. The temperature dependence of the line-width in the presence of an external radiation at a frequency of 9.49 GHz.

CONCLUSIONS

Using Kawabata's POT, in the CNT, we derived the line-profile formulas that show the relative frequency dependence of the absorption power and the temperature dependence of the line-width. We strictly used the commutation relation of annihilation and creation operators with using the Kubo identity. From the absorption power, on the order of 150, 200, 250, and 300 K, we can see the broadening effect of absorption power near the resonance peak, which exhibits a small increase as the temperature increase in the high-temperature region ($T > 200$ K). The line-width (the inverse of the spin relaxation) monotonically increases with increasing temperature ($T > 200$ K) due to the

interaction of electrons with acoustic phonons. The ESR scattering effect is little affected in low-temperature region ($T < 200$ K) because there is no correlation between the resonance field and Fermi-Dirac distribution function. The line-width obtained with POT agrees with the experimental result in low-temperature region. We conclude that the calculation process presented in this work is useful for studying the ESR in the CNT.

Acknowledgment

This research was supported by Basic Science Research Program through the National Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (NRF-2011-0027409). Also we thank the Suseong College Research Fund.

REFERENCES

1. Bachtold, P. Hadley, T. Nakanishi, C. Dekker, *Science* **294**, 1317 (2001).
2. O. Chauvet, L. Forro, W. Bacsa, D. Ugarte, B. Doudin, Walt A. de Heer, *Phys. Rev.* **B52**, R6963 (1995).
3. L. Forro et al, in "Science and Application of Nanotubes" (Tomanek, Enbody, Ed.), Kluwer Academic Publishers, New York, 2000.
4. A. Kawabata, *J. Phys. Soc. Jpn.* **29**, 902 (1970).
5. J. Y. Sug, S. D. Choi, *Phys. Rev.* **E55**, 314 (1996).
6. J. Y. Sug, S. G. Jo, S. D. Choi, *Phys. Rev.* **B64**, 235210 (2001).
7. J. I. Park, J. Y. Sug, H. R. Lee, *J. Kor. Phys. Soc.* **53**, 776 (2008).
8. J. I. Park, H. K. Lee, H. R. Lee, *J. Magnetism* **16**, 108 (2011).
9. R. Kubo, *J. Phys. Soc. Jpn.* **12**, 570 (1957).

10. J. P. Salvetat, T. Feher, L. Forro, *Phys. Rev.* **B72**, 75440 (2005).
11. A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, *Science* **273**, 483 (1996).
12. T. Ando, *J. Phys. Soc. Jpn* **74**, 777 (2005).
13. N. Sawaki, *J. Phys.* **C16**, 4611 (1983).