PHYSICAL REVIEW B VOLUME 52, NUMBER 12 15 SEPTEMBER 1995-II

Nonlinear optical properties of the substituted fullerenes $C_{59}X$ (X =B,N)

Jinming Dong
National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210008, People's Republic of China
and Center for Advanced Studies in Science and Technology of Microstructures, Nanjing 210093, People's Republic of China

Jie Jiang
Department of Physics, Nanjing University, Nanjing 210008, People's Republic of China

J. Yu
Department of Physics and Astronomy, Concurrent Computing Laboratory for Materials Simulations, Louisiana State University,
Baton Rouge, Louisiana 70803-4001

Z. D. Wang
Department of Physics, University of Hong Kong, Pokfulam Road, Hong Kong

D. Y. Xing
Department of Physics, Nanjing University, Nanjing 210008, People's Republic of China

(Received 7 April 1995)

Using the extended Su-Schrieffer-Heeger model and the sum-over-state method, we have calculated the third-order nonlinear polarizability γ and its dispersion spectra for single substituted fullerenes $C_{59}X$ (X=B or N atoms). Obtained results indicate that the substitute doping increases rather heavily the γ value, both the static and the dynamical response peak values. For $C_{59}N$, the highest peak value of γ (at $3\omega \sim 0.96$ eV) is found to be about 30 times larger than that for pure C_{60}, which may be important for its practical use.

Recently, pure and doped C_{60} have been intensively investigated[1–8] because they can show superconductivity with rather high critical temperature T_c[$=28$ K for Rb_3C_{60}) (Ref. 2)] and strong nonlinear optical properties.[3–8] The latter, perhaps, is the more interesting property. Up to now, the nonlinear optical response of the fullerenes has already been studied by many different experimental techniques from degenerate four-wave mixing[4] (DFWM) and third-harmonic generation[5] (THG) to electric-field-induced second-harmonic generation (EFISHG).[6] It has been found that the off-resonance third-order polarizability value γ is around 10^{-33} esu (Refs. 6 and 7) (7.5×10^{-34} esu for C_{60} and 1.3×10^{-33} esu for C_{70}) although there are discrepancies among existing experimental measurements and a higher value of $\gamma\sim10^{-30}$ esu was also reported for C_{60}.[4] Theoretical calculations[9,10] seem to support the smaller one obtained by most of the experiments. From these results, the γ values of the fullerenes are obviously about two orders of magnitude smaller than those of linear conducting polymers. However, as pointed out by Kajzar *et al.*,[8] quasi-one-dimensional conjugated polymers have residual infrared (ir) absorption due to overtones of *C-H* stretching vibrations, which limits their applications in optical communications. The fullerenes are composed of only carbon atoms and have no hydrogen atoms, which makes them promising materials to be applied in photonics devices. It is important to find a way to increase their γ values.

It is well known that the lattice and electronic structures of C_{60} change with doping.[11] Besides the usual alkali-metal doping, there is also substitute doping for the C_{60} molecule, i.e., one or more carbon atoms of the C_{60} molecule are substituted by other atoms.[12] Many kinds of modified C_{60} molecules $C_{60-m-n}X_mY_n$ have been synthesized, where X and Y represent the boron, nitrogen, or other possible substitute atoms, and n and m range from zero to a possible maximum value ≤ 6.[13] Theoretical calculations[13,14] demonstrate that the band gaps and electronic polarizations of the substituted fullerenes vary greatly with different substitute doping. Also, distribution of the π electrons on the C_{60} ball is changed by the substitute doping and the originally delocalized π electrons in pure C_{60} become more localized around the substituted atoms. All these factors will have a large effect on their nonlinear optical properties. Therefore it is interesting and useful to investigate theoretically this effect from the viewpoint of practical applications. In this paper we will perform a numerical calculation of the third-order nonlinear polarizability for the single substituted fullerenes $C_{59}X$ by using the extended Su-Schrieffer-Heeger (SSH) model[15] which has been successfully used to describe the pure, non-substitute-doped C_{60} system.[16–19] It has also been employed recently by us to study the structural and electronic properties of the substituted fullerenes $C_{60-n}X_n$ and the calculated results are reasonable and compatible with those obtained by

0163-1829/95/52(12)/9066(5)/$06.00

the self-consistent-field molecular-orbital (SCF-MO) method.[14]

The extended SSH model for the substituted fullerenes $C_{59}X$ can be written as

$$H=H_0+H_1\ , \tag{1a}$$

$$H_0=\sum_{\substack{\langle ij\rangle,s\\ \text{C-C}}}(-t_0-\alpha y_{ij})(c^{\dagger}_{i,s}c_{j,s}+\text{H.c.})+\frac{K}{2}\sum_{\substack{\langle ij\rangle\\ \text{C-C}}}y^2_{i,j}\ , \tag{1b}$$

$$H_1=\sum_{\substack{\langle ij\rangle,s\\ X\text{-C}}}(-t_1-\alpha_1 y_{ij})(c^{\dagger}_{i,s}c_{j,s}+\text{H.c.})+\frac{K_1}{2}\sum_{\substack{\langle ij\rangle\\ X\text{-C}}}y^2_{ij}\ . \tag{1c}$$

Here, the sum $\langle i,j\rangle$ is taken over the nearest neighbors, for both the C-C bonds in H_0 and the X-C bonds in H_1, t_0 and t_1 represent the hopping integrals for the C-C and X-C bonds, respectively, and similarly α and α_1 are the electron-phonon coupling constants related to the C-C and X-C bonds, respectively. Finally, K and K_1 are the spring constants corresponding to the C-C and X-C bonds, respectively. Since there is only one substituted impurity atom in $C_{59}X$, H_1 plays a perturbational role, and as an approximation the three original empirical parameters t_0, α, and K in H_0 are assumed not to change due to the substitute doping and taken to be the same in this numerical calculation as those in the pure C_{60} system: $t_0=2.5$ eV, $\alpha=6.31$ eV/Å, and $K=49.7$ eV/Å^2. Equation (1) can be solved by the standard adiabatic approximation method and the one-electron energy ε_k and corresponding electronic wave function $Z_{k,s}$ found. The choice of the three parameters t_1,α_1, and K_1 for the X-C bonds is of course important. The best way to do it, probably, is to determine them by comparison between theoretical calculated nonlinear optical polarizabilities and the experimentally observed ones for $C_{59}B$ and $C_{59}N$. But, to our knowledge, there has not been an experimental measurement of the nonlinear optical properties for these substituted doped fullerenes, not even linear optical absorption measurements. Fortunately, Kurita *et al.* [13] used the self-consistent-field molecular-orbital (SCF-MO) method to calculate the molecular structure and electronic properties for $C_{59}X$ and $C_{58}X$(X = B,N). We attempted to use the extended SSH model to investigate the structural and electronic properties of the same substituted doped fullerenes by carefully adjusting the values of the three parameters t_1, α_1, and K_1. We found that our numerical calculations can accurately reproduce the results obtained from the SCF-MO method if t_1, α_1, and K_1 are taken as the following values: $t_1=1.025$ eV, $\alpha_1=5.8$ eV/Å, $K_1=49$ eV/Å^2 for $C_{59}B$ and $t_1=0.95$ eV, $\alpha_1=6.0$ eV/Å, $K_1=48$ eV/Å^2 for $C_{59}N$.[14] Therefore, in this numerical calculation of the nonlinear optical properties, we adopt the same values of all the parameters for both $C_{59}B$ and $C_{59}N$. Of course, after more experimental observations are made for these substituted doped materials, it will be possible to determine more accurately all the parameter values in our model.

Within the independent electron approximation and sum-over-states (SOS) approach, the third-order polarizability γ can be expressed as[10,20]

$$\gamma(-3\omega;\omega,\omega,\omega)=\gamma_1+\gamma_2+\gamma_3+\gamma_4+\gamma_5\ , \tag{2}$$

$$\gamma_1(-3\omega;\omega,\omega,\omega)=2\sum_{\substack{l,m,n\in\text{occ}\\ p\in\text{unocc.}}}\mu_{pn}\mu_{nm}\mu_{ml}\mu_{lp}S_1(\omega)\ ,$$

$$S_1(\omega)=\frac{1}{(\epsilon_{pn}-3\omega)(\epsilon_{pm}-2\omega)(\epsilon_{pl}-\omega)}+\frac{1}{(\epsilon_{pn}+\omega)(\epsilon_{pm}+2\omega)(\epsilon_{pl}-\omega)}$$
$$+\frac{1}{(\epsilon_{pn}+\omega)(\epsilon_{pm}-2\omega)(\epsilon_{pl}-\omega)}+\frac{1}{(\epsilon_{pn}+\omega)(\epsilon_{pm}+2\omega)(\epsilon_{pl}+3\omega)}\ ,$$

$$\gamma_2(-3\omega;\omega,\omega,\omega)=2\sum_{\substack{l,m,n\in\text{unocc.}\\ p\in\text{occ.}}}\mu_{pn}\mu_{nm}\mu_{ml}\mu_{lp}S_2(\omega)\ ,$$

$$S_2(\omega)=\frac{1}{(\epsilon_{np}-3\omega)(\epsilon_{mp}-2\omega)(\epsilon_{lp}-\omega)}+\frac{1}{(\epsilon_{np}+\omega)(\epsilon_{mp}+2\omega)(\epsilon_{lp}-\omega)}$$
$$+\frac{1}{(\epsilon_{np}+\omega)(\epsilon_{mp}-2\omega)(\epsilon_{lp}-\omega)}+\frac{1}{(\epsilon_{np}+\omega)(\epsilon_{mp}+2\omega)(\epsilon_{lp}+3\omega)}\ ,$$

$$\gamma_3(-3\omega;\omega,\omega,\omega)=-2\sum_{\substack{p,l\in\text{occ.}\\ m,n\in\text{unocc.}}}\mu_{pn}\mu_{nm}\mu_{ml}\mu_{lp}S_3(\omega)\ ,$$

$$S_3(\omega)=\frac{1}{(\epsilon_{np}-3\omega)(\epsilon_{mp}-2\omega)(\epsilon_{ml}-\omega)}+\frac{1}{(\epsilon_{np}+\omega)(\epsilon_{mp}+2\omega)(\epsilon_{ml}-\omega)}$$

$$+\frac{1}{(\epsilon_{np}+\omega)(\epsilon_{mp}-2\omega)(\epsilon_{ml}-\omega)}+\frac{1}{(\epsilon_{np}+\omega)(\epsilon_{mp}+2\omega)(\epsilon_{ml}+3\omega)} ,$$

$$\gamma_4(-3\omega;\omega;\omega;\omega)=-2\sum_{\substack{p,l\in\text{occ.}\\ m,n\in\text{unocc.}}}\mu_{pn}\mu_{nm}\mu_{ml}\mu_{lp}S_4(\omega) ,$$

$$S_4(\omega)=\frac{1}{(\epsilon_{np}-3\omega)(\epsilon_{nl}-2\omega)(\epsilon_{ml}-\omega)}+\frac{1}{(\epsilon_{np}+\omega)(\epsilon_{nl}+2\omega)(\epsilon_{ml}-\omega)}$$

$$+\frac{1}{(\epsilon_{np}+\omega)(\epsilon_{nl}-2\omega)(\epsilon_{ml}-\omega)}+\frac{1}{(\epsilon_{np}+\omega)(\epsilon_{nl}+2\omega)(\epsilon_{ml}+3\omega)} ,$$

$$\gamma_5(-3\omega;\omega,\omega,\omega)=-2\sum_{\substack{m,p\in\text{unocc.}\\ n,l\in\text{occ.}}}\mu_{lp}\mu_{pn}\mu_{nm}\mu_{ml}S_5(\omega) ,$$

$$S_5(\omega)=\frac{1}{(\epsilon_{pl}-3\omega)(\epsilon_{pn}-\omega)(\epsilon_{ml}-\omega)}+\frac{1}{(\epsilon_{pl}+\omega)(\epsilon_{mn}+\omega)(\epsilon_{ml}+3\omega)}$$

$$+\frac{1}{(\epsilon_{pl}+\omega)(\epsilon_{mn}+\omega)(\epsilon_{pn}-\omega)}+\frac{1}{(\epsilon_{pl}+\omega)(\epsilon_{pn}-\omega)(\epsilon_{ml}-\omega)} .$$

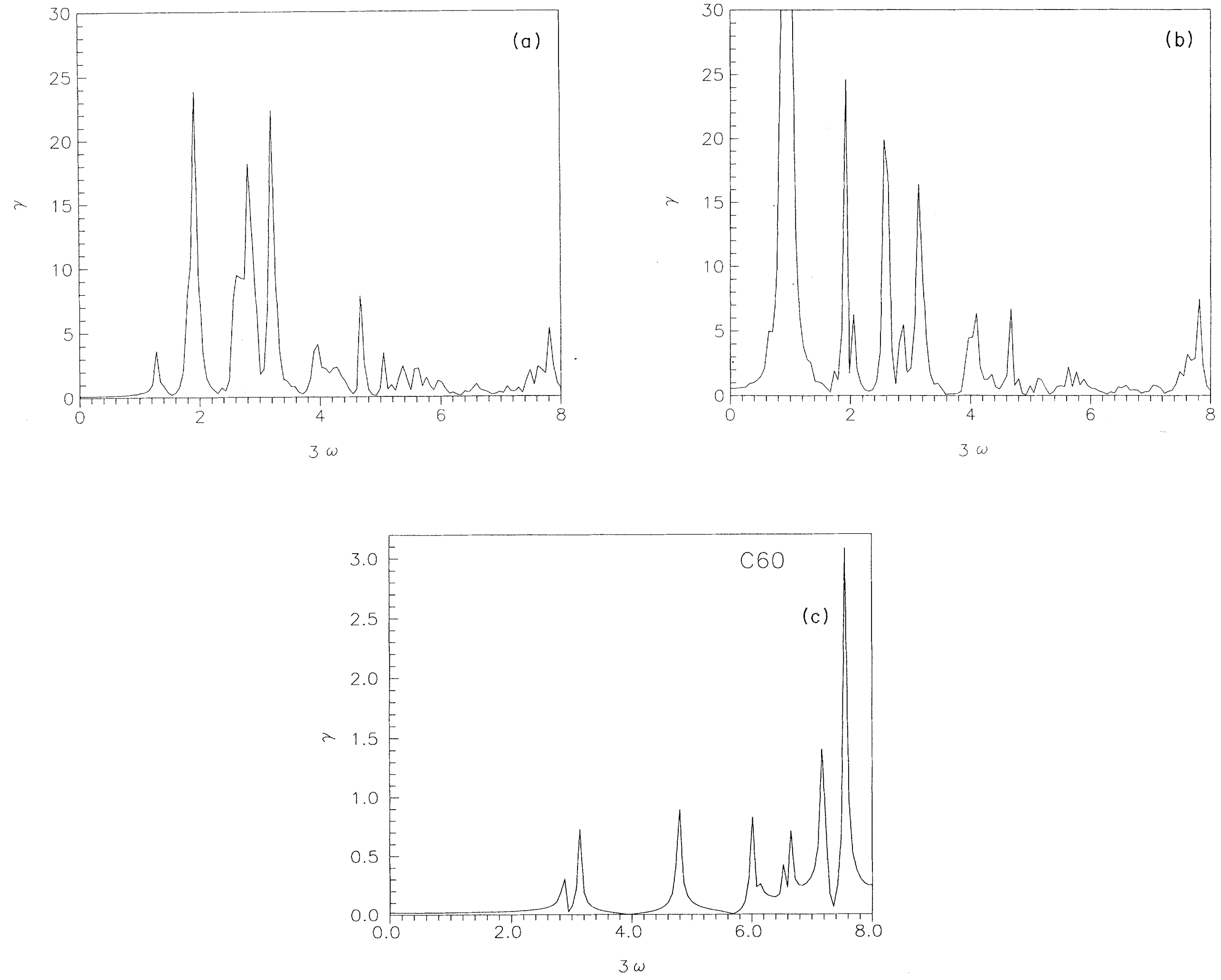

FIG. 1. The third-order polarizability γ spectra for $C_{59}X$ and C_{60} (in 10^{-32} esu). The unit of the x coordinate is eV. (a) $C_{59}B$; (b) $C_{59}N$; (c) C_{60}.

In the above formulas, ϵ_p is the one-electron energy, $\epsilon_{pn}=\epsilon_p-\epsilon_n$, and μ_{pn} is the dipole transition matrix between the one-electron states $Z_{p,s}$ and $Z_{n,s}$. In the extended SSH model, the dipole matrix element $\langle n|\mu_\alpha|m\rangle$ is given by

$$\langle n|\mu_\alpha|m\rangle=\sum_{j,s}{}' Z^*_{n,s}(j)(-e\alpha_j)Z_{m,s}(j)\ . \qquad (3)$$

In actual numerical calculation, a lifetime broadening factor η should be included in the denominator of Eq. (2), which suppresses the height of the resonant peaks, and is taken to be 1.68×10^{-2} eV in our calculation. Equations (1)–(3) are our basic equations used to calculate $\gamma(-3\omega;\omega,\omega,\omega)$ for pure C_{60} and $C_{59}X$.

The third-order nonlinear polarizability γ is calculated based upon the electronic structure obtained in the extended SSH model, and its static values are listed in Table I. Here, the z axis is taken along the direction from the pentagon at the bottom of the molecule to the pentagon at the top, and the x axis is directed to the impurity ion X. Since the ratios between the different components of γ are not known, a spatial average of γ is also given as $\gamma_{\mathrm{av}}=\frac{1}{5}[\gamma_{xxxx}+\gamma_{yyyy}+\gamma_{zzzz}+2(\gamma_{xxyy}+\gamma_{yyzz}+\gamma_{zzxx})]$. For comparison, the γ values of pure C_{60} are listed in Table I, too. From Table I, we can see that the static γ_{av} value of $C_{59}B$ and $C_{59}N$, respectively, is about six and 35 times larger than that of pure C_{60}, indicating that the substitute doping greatly increases the nonlinear optical polarizability of the C_{60} system. Also, owing to the distortion of the π electron distribution in the $C_{59}X$ molecule, especially around the substituted dopant B and N atoms,[14] the difference between the z and x (or y) components of γ for $C_{59}X$ is much more pronounced than that for pure C_{60}.

In addition, the dynamic nonlinear optical response of $C_{59}X$ has also been investigated by calculating the THG spectrum, and the results are shown in Fig. 1. For comparison, the dispersion of the linear polarizability $\alpha(\omega)$ of $C_{59}X$ is calculated and shown in Fig. 2. The highest peak in the γ spectrum of $C_{59}B$ is located at $3\omega=1.92$ eV and its γ value is about 24×10^{-32} esu, which is about 8 times larger than the corresponding highest peak value in pure C_{60}. Compared with the situation in the pure C_{60} molecule, all the peak positions and heights for $C_{59}B$ are changed. Similar to those in pure C_{60}, these peaks are also produced by two- or three-photon resonances. Major peaks can be assigned as three-photon resonances and are located at about $3\omega=1.28$, 1.92, 2.8, and 3.2 eV. The two-photon peaks with larger intensities are located at about $3\omega=1.92$, 2.64, and 3.96 eV. It is noted that there are three big peaks with very much larger strengths at $3\omega\sim1.92$, 2.8, and 3.2 eV in the spectrum. Most probably, they are caused by the following two effects. One is the large single-photon absorption intensities at the same energies as shown in Fig. 2(a), and the other is double resonance enhancement occurring at $3\omega=1.92$, 2.8, and 3.2 eV. The THG spectrum of $C_{59}N$ is shown in Fig. 1(b). The main differences between $C_{59}N$ and $C_{59}B$ concentrated in the lower energy region. For $C_{59}N$, three-photon resonances are located at about $3\omega=0.96$, 1.92, 2.56, and 3.14 eV and higher two-photon peaks are located at about $3\omega=2.04$, 2.88, and 4.09 eV. The four much larger

TABLE I. SSH-SOS theoretical static third-order polarizability γ (in 10^{-36} esu) tensor components for $C_{59}X$ and C_{60}.

γ	$C_{59}B$	$C_{59}N$	C_{60}
γ_{xxxx}	1570.80	−634.76	319.97
γ_{yyyy}	397.21	−485.31	319.97
γ_{zzzz}	2311.68	23 503.39	319.97
γ_{xxyy}	−151.65	−157.69	−22.95
γ_{yyzz}	355.24	5200.38	−22.95
γ_{zzxx}	257.48	−1868.51	−22.95
γ_{av}	1040.36	5746.39	164.44

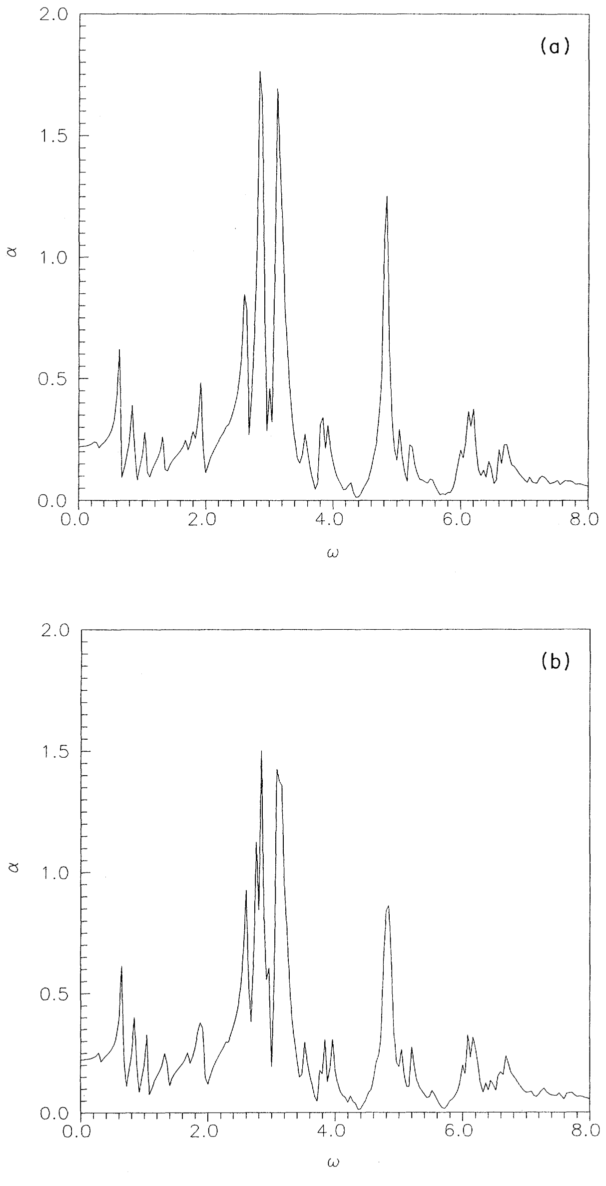

FIG. 2. The linear polarizability α spectra of $C_{59}X$ (in 10^3 Å^3). The unit of the x coordinate is eV. (a) $C_{59}B$; (b) $C_{59}N$.

strengths at $3\omega \sim 0.96$, 1.92, 2.56, and 3.14 eV can also be explained as large single-photon absorption intensities [see Fig. 2(b)] and double resonance enhancement. The highest peak in the spectrum is located at $3\omega = 0.96$ eV and its value is about 85×10^{-32} esu, which is about four times larger than the highest peak value in $C_{59}B$ and 30 times larger than that for pure C_{60}.

It is well known that the rather larger nonlinear optical response for the C_{60} system is mainly produced by its delocalized π electrons as in conjugated polymer chains. However, the three-dimensional character of the C_{60} molecule causes severe limitations on its nonlinear optical properties and makes its γ values become about two orders of magnitude smaller than those of linear polymers containing a similar number of carbon atoms. From calculation with the extended SSH model, it is known that the substituted dopant ions X attract or repel electrons and cause a distortion of the π electron distribution on the C_{60} molecule surface, which mainly happens around the dopant ions.[14] This effect can be called an inductive effect. In addition, the dopant X ions cause greater localization of the original delocalized π electrons around them,[14] and so maybe reduce the effective space dimensions of the C_{60} molecule. In our opinion, these two effects make the nonlinear optical properties of $C_{59}X$ different from pure C_{60} and enlarge rather greatly the γ values of $C_{59}X$. It has been found[14] that the localization effect of the N impurity atom is stronger than that of the B atom. So the inductive effect and the reduction effect of the effective space dimensions in $C_{59}N$ are stronger, which may explain why $C_{59}N$ has larger γ values than $C_{59}B$. Therefore it will be interesting to see what would happen if heavier substitute doping of C_{60} is done. Based upon the calculated result in this paper, most probably this process will raise the γ value further. Work along this direction is in progress.

This work was supported by the Natural Science Foundation in Jiangsu Province of China. Z. D. W. acknowledges partial support by a RGC research grant of Hong Kong.

---

[1] H. W. Kroto *et al.*, Chem. Rev. **91**, 1213 (1991); W. Krätschmer *et al.*, Nature **347**, 354 (1990); S. Saito and A. Oshigama, Phys. Rev. Lett. **66**, 2637 (1991).

[2] A. F. Hebard *et al.*, Nature **350**, 600 (1991); M. J. Rosseinsky *et al.*, Phys. Rev. Lett. **66**, 2830 (1991).

[3] C. T. Chen, *et al.*, Nature **352**, 603 (1991); C. Reber *et al.*, J. Phys. Chem. **95**, 2127 (1991).

[4] W. J. Blau *et al.*, Phys. Rev. Lett. **67**, 1423 (1991).

[5] Q. Gong *et al.*, J. Appl. Phys. **71**, 3025 (1992); H. Hoshi *et al.*, Jpn. J. Appl. Phys. **30**, L1397 (1991).

[6] Y. Wang and L. T. Cheng, J. Phys. Chem. **96**, 1530 (1992); Y. Wang, G. F. Bertsch, and D. Tomanek, Z. Phys. D **25**, 181 (1993).

[7] Z. H. Kafafi *et al.*, Phys. Rev. Lett. **68**, 2705 (1992); Chem. Phys. Lett. **188**, 492 (1992).

[8] F. Kajzar *et al.*, Synth. Met. **54**, 21 (1993); J. S. Meth *et al.*, Chem. Phys. Lett. **197**, 26 (1992); Phys. Rev. Lett. **73**, 1617 (1994).

[9] K. Harigaya and S. Abe, Jpn. J. Appl. Phys. **31**, L253 (1992).

[10] Z. Shuai and J. L. Bredas, Phys. Rev. B **46**, 16 135 (1992).

[11] T. Kato *et al.*, Chem. Phys. Lett. **180**, 446 (1991); T. Takahashi *et al.*, Phys. Rev. Lett. **68**, 1232 (1992); P. A. Lane *et al.*, *ibid.* **68**, 887 (1992).

[12] T. Guo *et al.*, J. Phys. Chem. **95**, 4948 (1991); Y. Chai *et al.*, *ibid.* **95**, 7564 (1991).

[13] N. Kurita *et al.*, Phys. Rev. B **48**, 4850 (1993); N. Kurita *et al.*, Chem. Phys. Lett. **198**, 95 (1992).

[14] Jinming Dong, Jie Jiang. Z. D. Wang, and D. Y. Xing, Phys. Rev. B **51**, 1977 (1995); M. Liu, Z. D. Wang, Jinming Dong, and D. Y. Xing, Z. Phys. B **97**, 433 (1995).

[15] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. B **22**, 2099 (1980).

[16] K. Harigaya, J. Phys. Soc. Jpn. **60**, 4001 (1991); Phys. Rev. B **45**, 13 676 (1992); **48**, 2765 (1993).

[17] B. Friedman, Phys. Rev. B **45**, 1454 (1992); B. Friedman and Jaewan Kim, *ibid.* **46**, 8638 (1992); Jaewan Kim and W. P. Su, *ibid.* **50**, 8832 (1994).

[18] R. L. Fu, R. T. Fu, and X. Sun, Phys. Rev. B **48**, 17 615 (1993).

[19] C. L. Wang, W. Z. Wang, and Z. B. Su, Phys. Rev. B **49**, 17 468 (1994).

[20] J. Yu, Ph.D. dissertation, Dept. of Physics, University of Houston, 1991.