

Theoretical Raman spectroscopy study of finite and infinite fullerene chains inside single-walled carbon nitride nanotubes

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Abstract. We investigated the hybrid system between Nitrogen doped Single Wall Carbon Nanotubes (N-SWCNT) and fullerene (C_{60} C_{70}) molecules. The structure of the encapsulated fullerenes inside N-SWCNTs is derived from minimum energy calculation using a convenient Lennard-Jones expression of the Van der Waals intermolecular potential. The nonresonant Raman spectra of peapods are studied by using Raman spectroscopy. The dependence of the Raman spectra as a function of the nanotube diameter is discussed. The relative Raman intensity from the C_{60} to that from the tube as a function of the fullerene concentrations is analyzed. These results are useful for the interpretation of the future experimental Raman spectra of C_{60} and C_{70} carbon nitride peapods.

Keywords: Nanotube, nitrogen, doped, fullerene, peapods, Raman spectroscopy.

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1 Introduction

The molecular arrays of fullerenes inside single wall carbon nanotubes (SWCNTs) are known as peapods. The first observations of peapods took place in 1998 and the visual appearance by electron microscopy recalling small weights inside the tubes [1]. The craze aroused by this discovery was very important, and a year later was published a mode of synthesis [2] to produce these objects in sufficient quantities. With the increasing improvement of the diameter control of nanotubes produced, methods of production of peapods of very high quality could be developed [3]. Similar to SWCNTs, N-SWCNT can also be filled with fullerene molecules such as C_{60} and C_{70} , so-called carbon nitride peapods ($C_n@N\text{-SWCNT}$, $n=60,70$).

The enthusiasm of the scientific community for these objects can be explained by many reasons. From a fundamental point of view first of all, the possibility of "artificially" producing almost one-dimensional crystals through the C_{60} stack is a unique opportunity to study the physics of these particular phases. Note also that the study of the influence of confinement inside nanotubes on the physics of C_{60} is of interest.

From the applications point of view, calculations of the band structure calculations [4] of the peapods concluded to the existence of superconducting phases with critical temperature of these compounds and was even measured at 40 K in

C₆₀ phases doped with cesium [5]. The unidimensional structure of the C₆₀s and C₇₀s in the peapods could help to increase this critical temperature.

Many applications have been envisaged for peapods especially in the field of molecular electronics. It was observed that C₆₀ could move inside the nanotubes under the effect of the electron irradiation of a transmission microscope [1]. The idea of nano-interrupter then came into being, as was the possibility of making a memory storage medium based on the position of the C₆₀s in the tubes. Concerning the mechanical properties, the insertion of C₆₀ inside the tubes should make it possible to stiffen the material and make it less deformable when radial stress is applied.

We have previously studied the different possible configurations of C₆₀ and C₇₀ molecules encapsulated into SWCNTs and Boron nitride nanotubes with diameter lower than 1.50 nm. Raman spectra of the obtained peapods have been calculated within the bond-polarizability model [5,6]. Our results were in qualitative agreement with others studies ones [8,9,10]. Here, in order to complete our study of peapods, we present the calculation results obtained in the case of C₆₀ and C₇₀ molecules encapsulated into SWCNNTs. Our work addresses new questions as to the influence of the nanotube diameter and the C₆₀ and C₇₀ filling rate. In this context, we use a direct diagonalization of the dynamical matrix for small peapods and the spectral moment method for larger ones. We report the structural and vibrational properties C₆₀@SWCNNT as a function of nanotube diameter and the chirality.

2 Models and method

SWCNTs are obtained by rolling a single hexagonal graphene sheet and can be specified by integers (n,m). The chiral vector C_h makes an angle, called the chiral angle. For an ideal tube, the diameter d and chiral angle θ are given by the following relations:

$$d = \frac{a}{\pi} \sqrt{n^2 + m^2 + mn}, \theta = \arctan\left(\frac{2n + m}{2\sqrt{n^2 + m^2 + mn}}\right)$$

Where a is the lattice constant of 2D graphene sheet. The number of hexagons, N , contained within the 1D unit cell of a nanotube is determined by $N = \frac{2(m^2 + n^2 + nm)}{d}$

The nitrogen atoms are incorporated in the SWCNTs by substitution generated structure of single walled carbon nitride nanotubes (SWCNNTs) and the N doping sites were distributed on the surface of the tube in such way that the N-N separation is greater than 0.48 nm. The doping rate is defined by 10 nitrogen atomic percent, which gives the percentage of nitrogen atom relative to the total number of atoms in the tube.

C₆₀ and C₇₀ are a closed-cage molecule consisting of sixty and seventy carbon atoms respectively. Two different C-C bond lengths of 0.140 and 0.146 nm exist in C₆₀ and C₇₀.

The configuration of the guest C₆₀ and C₇₀ molecules inside SWCNNTs is derived from energy calculations performed using the same procedure described in our previous calculations for carbon Boron nitride peapods [6-7,10]. Depending on the nanotube diameter, different configurations of C₆₀ and C₇₀ can certainly exist. In this work we restrict our study by considering only a linear chain of C₆₀ and C₇₀ confined inside SWCNNT Figure 1.

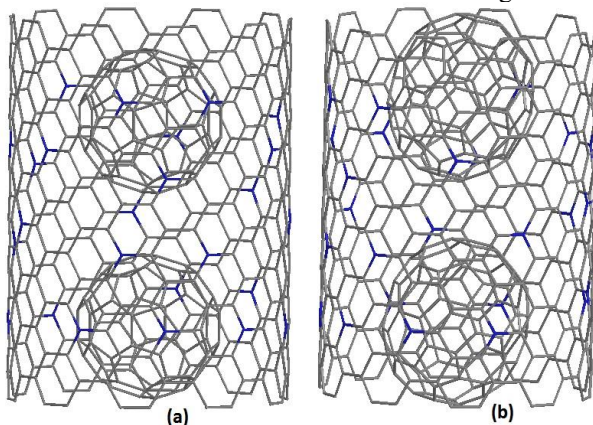


Figure 1: Structure of two SWCNNT peapods: (a) C₆₀@(10,10) and (b) C₇₀@ (10,10).

The C-C interaction between carbon atoms belonging to non-bonded fullerenes, and between fullerenes and the surrounding nanotube, are represented by the Lennard-Jones potential:

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

. The parameter ϵ_{ii} of nitrogen and carbon atom is 0.006281 eV and 0.002635 eV, and σ_{ii} is 0.3365 nm and 0.3369 nm, respectively [12].

The parameters ϵ_{ij} and σ_{ij} between different particles are calculated by the following Lorentz-Berthelot rules.

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \quad \text{and} \quad \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$$

The intratube interactions C-C and C-N at the surface of the SWCNNT are described by using the same force constant as used in recent calculations of the Raman spectra of SWCNNT of different lengths. The C-C intramolecular interactions between carbon atoms at the surface of C_{60} molecules are modeled by the force constants model described by Jishi and Dresselhaus [13]. The dynamical matrix of free C_{70} molecule was calculated using the density functional theory (DFT) as implemented inside the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) package [14]. The dynamical matrix of peapods is built block by block from the dynamical matrices of each subsystem: the dynamical matrix of the tube and fullerenes forms the bidiagonal block of the dynamical matrix of the peapod, while the dynamical matrix associated with the tube–fullerenes and fullerenes–fullerenes interactions forms the off-diagonal block.

The intensities of the Raman lines were calculated within the empirical nonresonant bond polarizability model [15]. Raman spectra are calculated using direct diagonalization of the dynamical matrix for small samples (few hundreds atoms). However when the system contains a large number of atoms, the dynamical matrix is very large and its diagonalization fails or requires long computing time. In contrast, the spectral moments method allows to compute directly the Raman spectrum of very large harmonic systems without any diagonalization of the dynamical matrix [16-17]. This same approach was recently used in our previous calculations [8-9]. In all our calculations, the nanotube axis is along the Z axis and a carbon atom of the SWCNT is along the X axis of the nanotube reference frame. The x, y, and z are the axes of the laboratory frame, and the laser beam is assumed to be along the y axis. We consider that both incident and scattered polarizations are along the Z axis to calculate the polarized ZZ spectra.

3 RESULTS AND DISCUSSION

We report the results of the calculated Raman spectra for completely filled SWCNNTs. The dependence of the Raman spectrum as a function of diameter of the nanotube is considered. Finally, the effect of average filling factor of C_{60} and C_{70} are considered.

3.1. Optimized structure of C_{60} CN peapods

First, we calculated the minimum energies of Lennard-Jones C_{60} -SWCNNT and C_{60} - C_{60} interactions in order to obtain the optimal structure of the inserted fullerene molecules inside the tube. For tube diameter lower than 1.48 nm, the energy minimizations the linear chain as being optimum for tubes having a diameter $D_{\text{tube}}=2(R+d)$, where R is the C_{60} fullerene radius and d the interlayer C_{60} -SWCNNT distance, varies from 0.3 to 0.35 nm (Table 1). The optimal C_{60} - C_{60} gap inside SWCNNTs is calculated around 1.0 ± 0.05 nm for all optimized peapods. In our previous works [6-7], focused on carbon peapods C_{60} @SWCNTs only, we have found that the C_{60} molecules adopt a linear configuration for diameters below 1.45 nm, the same results are found for BN [10].

Table 1: Optimized structural parameters of the C₆₀ molecules inside SWCNT in diameter range where the C₆₀ molecules form a linear chain inside nanotubes. Our calculations show that this angle is dependent on the nanotube diameter. However, for the same diameter, θ does not significantly depend on their chirality. (see Fig. 1 in Ref. [8] for a definition of the angle θ).

Tube Index (n,m)	Tube Diameter(nm)	Chiral Angle (Deg)	C ₆₀ -Tube Distance (nm)	C ₆₀ -C ₆₀ Distance(nm)
(11,8)	1.294	24.79	0.296	1.010
(12,7)	1.303	21.36	0.300	1.010
(13,6)	1.317	17.99	0.308	1.006
(17,0)	1.331	0	0.315	1.008
(14,5)	1.336	14.70	0.317	1.009
(10,10)	1.356	30	0.327	1.008
(15,4)	1.359	11.51	0.329	1.010
(12,8)	1.365	23.41	0.331	1.002
(14,6)	1.392	16.99	0.344	1.0101
(18,0)	1.410	0	0.347	1.006
(11,10)	1.425	28.42	0.361	1.007
(13,8)	1.438	22.17	0.365	1.010

3.2. Raman spectra of completely filled peapods

We calculated the Raman active modes in C₆₀ and C₇₀ CN peapods. For this purpose, we considered a peapods filled to saturation. Infinite peapods have been obtained by applying periodic conditions on unit cells both for tube and the fullerene molecules. The calculated ZZ Raman spectra of C₆₀@CN-(10,10), with their corresponding unfilled armchair nanotube (10,10) (tube diameter close to 1.37 nm) and the unoriented C₆₀ molecule are displayed in figure 2. Raman lines can be divided into three frequency ranges: (i) below 200 cm⁻¹ where the breathing-like modes (BLM) dominate (left), (ii) an intermediate range between 200 and 600 cm⁻¹ (middle), and (iii) above 1300 cm⁻¹ where the tangential-like modes (TLM) are located (right).

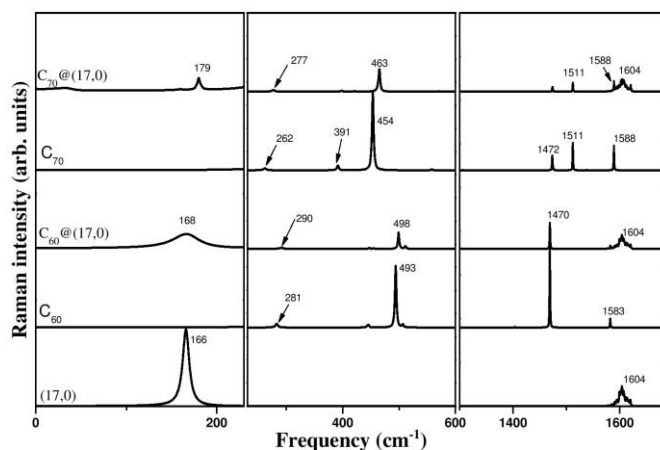


Figure 2: Calculated ZZ-polarized Raman spectra of infinite C₆₀@(17,0) and C₇₀@(17,0) peapods. Spectra of infinite empty (17,0), C₆₀ and C₇₀ molecules are also reported for references

In the BLM, we calculated an upshift of the RBM mode when the C₆₀ and C₇₀ molecules are encapsulated inside the tube. For instance, the RBM of the unfilled (17,0), tube shifts from 166 cm⁻¹ in empty (17,0) to 168 cm⁻¹ and 179 cm⁻¹ in completely filled C₆₀@(17,0) and C₇₀@(17,0) peapods respectively. This mode is assigned to the radial breathing like mode (RBLM) of the tube.

Concerning the main modes of SWCNNT, we observe that the TLM are almost not affected by the insertion of C_{60} and C_{70} molecules inside the nanotube.

Concerning the main modes of C_{60} and C_{70} molecules, the A_g mode of C_{60} located at 493 cm^{-1} shift to 498 cm^{-1} in $C_{60}@$ (17,0) peapod and the A_g mode of C_{60} located at 454 cm^{-1} shift to 463 cm^{-1} in $C_{70}@$ CN-(10,10) peapod, The same behavior observed for the H_g mode of C_{60} located at 281 cm^{-1} shift to 291 in $C_{60}@$ CN-(10,10) peapod and the H_g mode of C_{70} located at 262 cm^{-1} shift to 277 cm^{-1} in $C_{70}@$ (10,10) peapod . The upshift can be explained by the van der Waal intermolecular interactions acting between the fullerenes and the SWCNNTs.

3.3. Diameter and chirality dependence of the Raman spectrum of peapods

In this section, we focus on the low frequency range of the ZZ polarized Raman spectrum of CN peapods. We have investigated the dependence of some specific Raman active modes of infinite peapods as a function of the diameter of the nanotube. We already reported that the RBM region is the most influenced by the fullerene filling. The RBLM mode is also the most appropriate for extracting structural and dynamical information of nanotubes. Few years ago, in the framework of the bond polarization theory and using the spectral moments method, we have found, in agreement with different approaches [18-20], that in isolated tube, the relation gave the diameter D dependence of the RBM frequency: $\omega_{\text{RBM}}=a/D$, where $a=270\text{ nm cm}^{-1}$.

Figure 3 shows the evolution of the RBM and RBLMs frequencies of C_{60} peapods as function of the tube diameter (Figure 3 (a)) and the as the function of inverse diameter (Figure 3 (b)).

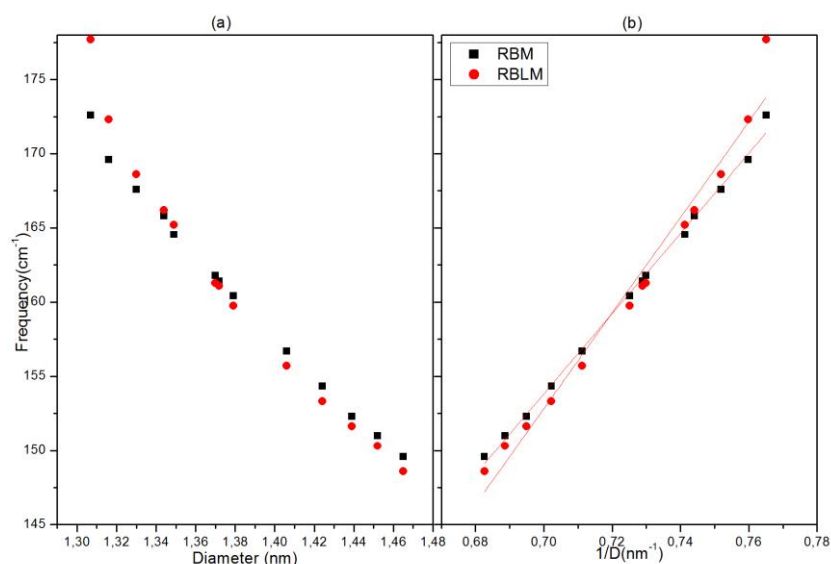


Figure 3: The calculated frequencies of the RBLM (circles) in isolated infinite C_{60} nanopeapod and the originating RBM (squares) in infinite unfilled tubes with diameter below 1.48nm.

The RBLM of peapod behavior is qualitatively the same as the RBM. It deviates from the law stated for the RBM frequency. The dependence of the frequency of the RBM and RBLM modes as a function of tube diameter is described by an $a/D+b$ scaling law, with $a = 363.6\text{ nm.cm}^{-1}$ and $b = 72.72\text{ cm}^{-1}$ for C_{60} peapods. This result is in agreement with results of undoped SWCNT peapods. We have found that the behavior of the RBLM mode with the SWCNT diameter was clearly modified in carbon peapods.

3.4. Raman spectra of incompletely C_{60} filled peapods

In real peapod samples, nanotubes are incompletely filled with C_{60} molecule and the highest filling rates range between 70% and 90% [3,21]. The exact degrees ranges from a certain percent to almost 100% filling. In the following, we make

the hypothesis of partial filling of the tubes with a quasi infinite long chain. Very long tubes are considered (more than 100 cells) and a defined number of molecules C_{60} are inserted. To avoid finite size effects, we applied periodic conditions to the tube. We found that the number of molecules inside the SWCNNT has no significant effect on the Raman spectrum except on the RBLM mode which is the most sensitive to the degree of filling of the SWCNNTs.

An illustration of the dependence of the ZZ polarized Raman spectra with the filling factor calculated for the $C_{60}@ (10,10)$ linear peapod (figure 4). The spectra are calculated for five values of the filling factor $F = 20, 40, 60, 80$ and 100% corresponding to 2, 4, 8, 12 and 16 molecules C_{60} , respectively, inside SWCNNTs.

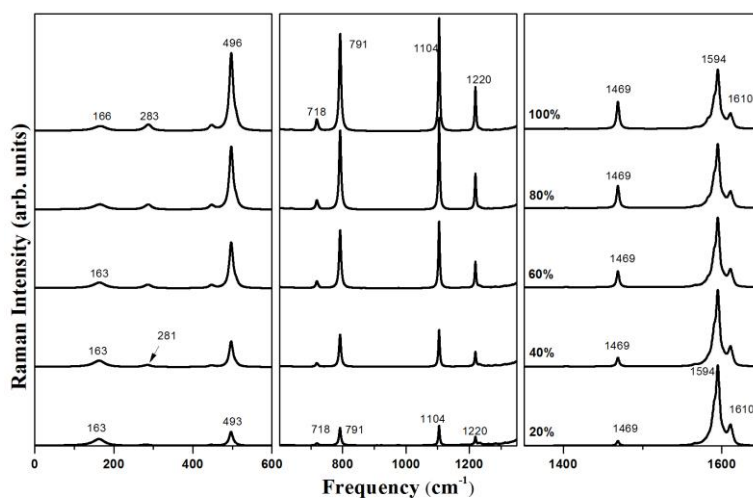


Figure 4: ZZ-polarized Raman spectra for infinite nanopeapods as a function of the C_{60} filling factor in $C_{60}@ (10,10)$.

The calculation results mainly illustrate the filling dependence of the Raman spectra profile. As expected, the filling level of C_{60} molecules inside the SWCNNTs has no significant effect on the Raman spectrum in the TLM range. In contrast, in the BLM range, all the Raman lines undergo a frequency upshift more or less significant as the filling factor increases. Similarly, the intensity of the C_{60} characteristic lines increases. A single RBLM peak characterizes all spectra for 20 and 100% of the filling factor. For $F=100%$ (high filling level) the RBLM peak is located at 166 cm^{-1} and at 163 cm^{-1} for $F=20%$ (low filling level). Let us call ω_h (mode located around 280 cm^{-1}) and ω_l (mode located around 160 cm^{-1}) the frequency of the heavy and light filling factor, the increase of F from 20 to 100% leads to the appearance of two peaks at frequency close to ω_h and ω_l . The intensity of these peaks shifts from the one located around ω_l to that located around ω_h when increasing F .

The lines around $281, 493 \text{ cm}^{-1}$ shifts to $283, 496 \text{ cm}^{-1}$ respectively and increases in intensity from 20 to 100% for $C_{60}@ (10,10)$. The observed frequency shift can be associated with C_{60} -SWCNNTs and C_{60} - C_{60} Van der Waals interaction effects.

Next, we have used the spectral moment's method to investigate the evolution of the average non resonant intensity ratios between Raman mode of C_{60} molecules and CN nanotube as a function of the concentration of molecules C_{60} inside the tube. Evidently, this nonresonant approach is not able to calculate the dependence of the absolute intensity of each mode with the excitation energies. However, the dependence of the Raman spectrum with the filling factor, the relative intensity ratio between a Raman mode of C_{60} and a mode of SWCNNT, normalized by the same ratio calculated for a reference filling factor, gives a useful method to derive from Raman experiments the relative concentration of C_{60} in peapods samples prepared with the same batch as that of the reference filling factor sample.

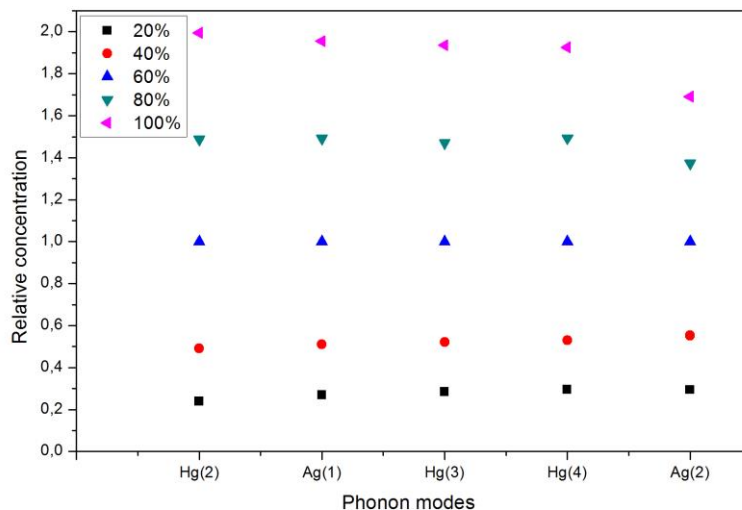


Figure 5: Calculated average intensity ratios, normalized on the 60% filling factor intensities, between modes of the C₆₀ in the C₆₀ @(10,10) peapod crystal and the RBLM (Hg(2), Ag(1), Hg(3), Hg(4)) or G-mode (Ag(2)) of the CN-(10,10) nanotube.

We calculate the dependence of the Raman spectrum at different filling factors. For each filling factor, the integrated intensity ratios between Raman mode of C₆₀ molecules and the RBLM (for C₆₀ phonon modes: Hg(2), Ag(1), Hg(3) and Hg(4)) or G-mode (for C₆₀ phonon mode: Ag(2)) are calculated. These calculated intensity ratios are normalized with respect to the same intensity ratios calculated for the 60% filling factor sample. The relative concentrations derived by this way are shown in figure 5. As expected, the relative concentrations calculated for low frequency modes expect the Ag(2) high frequency modes that could showing a overestimated concentration.

4 CONCLUSIONS

We have calculated the nonresonant Raman spectrum of isolated C₆₀ inside nitrogen doped nanotubes. For the tube investigated diameter range, the C₆₀ molecules adopt a linear arrangement for N-SWCNTs diameter lower than 1.48 nm. Then, For the obtained C₆₀ peapods, the dependence of the Raman spectrum with the diameter and the nanotube filling level have been analyzed. We found that the behaviour of the RBLM mode with the diameter was clearly modified in peapod. This involves that the linear relation between the RBLM frequency and the inverse of diameter found in SWCNNT will be modified in the case of peapod sample. Finally, we think that the calculated Raman spectra reported in the present work can be useful to understand the experimental Raman spectra of C₆₀ molecules inside N-SWCNTs.

References

1. B. W. Smith, M. Monthieux and D. E. Luzzi, *Nature*, **396**, 323-324 (1998)
2. B. Burteaux, A. Claye, B.W. Smith, M. Monthieux, D.E. Luzzi, and J.E. Fischer, *Chemical Physics Letters* **310**, 84, (1999).
3. H. Kataura, Y. Kumazawa, Y. Maniwa, I. Umez, S. Suzuki, Y. Ohtsuka, Y. Achiba, *Synth. Met.* **121**, 1195-1196 (2001).
4. R. Saito, G. Dresselhaus and M. S. Dresselhaus. Imperial college press, London, (1998).
5. T.T.M. Palstra, O. Zhou, Y. Iwasa, P.E. Sulewski, R.M. Feliming, and B.R. Zegarski. *Solide State Communications*, **93** :327, 1995
6. F. Fergani, S Abdelkader, H. Chadli, A. Rahmani. *OAJ Materials and Devices*, **3** pp.0803 (2018).
7. H. Chadli, F. Fergani, S Abdelkader, Ah Rahmani, B. Fakrach. *ISPDS1*, Dec 2015, Amiens, France.
8. H. Chadli, A. Rahmani, K. Sbai, P. Hermet, S. Rols, and J.-L. Sauvajol, *Phys. Rev. B* **74**, 205412 (2006).

9. H. Chadli, F. Fergani, M. Bentaleb, B. Fakrach, K. Sbai, A. Rahmani, J.-L. Bantignies, J.-L. Sauvajol, *Physica E* **71**, 31-38 (2015).
10. B. Fakrach, A.H Rahmani, M. Boutahir, H. Chadli, F. Fergani, P. Hermet and A. Rahmani, *Crystals*, **8**, 118 (2018).
11. J.W. Kang, H.J. Hwang, *J. Phys.: Condens. Mat.* **16**, 3901 (2004).
12. F. Darkrim, D. Levesque, *J. Chem. Phys.* **19**, 4981 (1998).
13. R. A. Jishi, R. M. Mirie, and M. S. Dresselhaus, *Phys. Rev. B* **45**, 13685 (1992)
14. J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejon, J. Sanchez-Portal, *J. Phys.: Condens. Matter*,**14**, 2745-2779 (2002).
15. Guha, S.; Menendez, J.; Page, J. B. and Adams, G. B. *Phys. Rev. B*, **53**, 13106 (1996).
16. C. Benoit, E. Royer, and G. Poussigue, *J. Phys.: Condens. Matter* **4**, 3125 (1992).
17. A. Rahmani, C. Benoit and G. Poussigue, *J. Phys.: Condens. Matter* ,**5** , 7941 (1993).
18. V. N. Popov, *Phys. Rev. B*, **67**, 085408 (2003).
19. L. Wirtz, A. Rubio, R.A de la Concha, A. Loiseau, *Phys. Rev. B*, **68**, 045425 (2003).
20. R. Akdim, R. Pachter, D. Xiaofeng and W.W. Adams, *Phys. Rev. B*, **67**, 245404 (2003).
21. M. Chorro, A. Delhey, M. Monthieux, P. Launois, *Phys. Rev. B*, **75**, 035416 (2007).

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