January 2009 Volume 5 Issue 1

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 5(1), 2009 [62-67]

Stability of Na metal clusters inside C_{84} and C_{60}

Ranjan Kumar[1]*, Harkiran Kaur[2]

[1]Deptt. of Physics, Panjab University, Chandigarh, (INDIA)

[2]U.C.I.M., Panjab University, Chandigarh, (INDIA)

E-mail : ranjan@pu.ac.in

Received: 23rd July, 2008 ; Accepted: 28th July, 2008

ABSTRACT

Fullerene is a hollow molecule of carbon atoms and may accommodate guest atoms inside it. Therefore a number of Na atoms may be doped inside it. We have used the model potential calculations to investigate the stability and charge transfer when Na atoms are doped inside C_{84} and C_{60}. In our calculations, the number of the Na atoms doped inside fullerene varies from 1 to 9 in case of C_{84} and 1 to 6 in case of C_{60}. The binding between Na atoms has been modeled using Gupta potential and Coulomb Potential. The interaction between Na atoms and fullerene molecule is modeled using exp potential and Coulomb Potential. The Minimization of total cohesive energy w.r.t to charge transfer and size of the cluster results in total charge transfer from sodium atom cluster in each energetically favorable case however different values of on shell coulomb repulsion V restricts the number of sodium atoms which can be doped inside fullerene molecule For all clusters, charge transfer is energetically favorable.

1. INTRODUCTION

Carbon, an element of prehistoric discovery, is very widely distributed in nature. It is found in abundance in the sun, stars, comets, and atmospheres of most planets. Carbon is one of the few elements known to man since antiquity. Graphite and diamond are the two well known allotropic forms of carbon, with markedly different physical properties. Diamond is a large-gap semiconductor. The non-conducting property follows from the sp^3 bonding scheme of the carbon atoms in the crystal structure. Graphite consists of parallel sheets of graphene, an sp^2 bonded honeycomb lattice of carbon atoms. A single graphene sheet would be a zero-gap semiconductor, but the interlayer interactions turn graphite into a semi-metal[1]. The discovery of fullerenes by Kroto and co-workers initiated a new era in carbon chemistry. Fullerenes were first discovered in 1985 in an apparatus designed by Prof. Rick Smalley to produce atomic clusters of the non-volatile element[2]. Fullerenes are a family of carbon allotropes, molecules composed entirely of carbon, in the form of a hollow sphere, ellipsoid, tube, or plane. Few new carbon structures include Single and Mutiwalled carbon nanotubes, Multi layered Carbon Onions etc.Spherical fullerenes are also called buckyballs, and cylindrical ones are called carbon nanotubes or buckytubes. Fullerenes are similar in structure to graphite, which is composed of a sheet of linked hexagonal rings, but may also contain pentagonal rings that would prevent a sheet from being planar. The smallest member of fullerene is C_{20} (dodecahedron) with 12 pentagons, no hexagons. The most common fullerene is C_{60}. The structure of C_{60} is a truncated icosahedron. There are 12 pentagonal faces and 20 hexagonal faces. Here, 60 carbon atoms are located at the vertices of each polygon and every carbon site is equivalent to every other site. The average nearest neighbor C-C distance in C_{60} is 1.44 Å[3] and each carbon

atom inside C_{60} is trigonally bonded to other carbon atoms. Another fairly common buckminsterfullerene is C_{70}, but fullerenes with 72, 76, 84 and even up to 100 carbon atoms are commonly obtained. Three dimensional assemblies of these molecules form solids which have very interesting electronic and mechanical properties. The chemical and physical properties of fullerenes have been of great interest in the field of research and development[4]. The fullerenes are also found to be soluble in common solvents such as benzene, toluene or chloroform solids based on buckyballs can be insulators, conductors, semiconductors, or even superconductors when doped with other atoms or molecules. Fullerenes and their derivatives are also applied to coat materials on some chemical sensors, such as quartz crystal microbalance (QCM) and surface acoustic wave sensors .Fullerenes can be used in the formation of polymeric materials. These polymers have possible applications to catalysts, electronic devices, and other area. Fullerenes are chemically reactive and can be added to polymer structures[5] to create new copolymers with specific physical and mechanical properties. Fullerenes are powerful antioxidants, reacting readily and at a high rate with free radicals, which are often the cause of cell damage. Experiments suggest that fullerenes which incorporate alkali metals possess catalytic properties.

Fullerenes can be doped in several different ways which includes: *Endohedral Doping*-where the dopant goes into the hollow core of the fullerene. *Substitutonal Doping*-where the dopant replaces one or more of the carbon atoms on the shell of the molecule. *Exohedral Doping*-where the dopant is outside the or between fullerene shells. Endohedral doping is the addition of an atom or an ion into the interior hollow core of the fullerene molecule to form an endohedrally doped molecular unit, also called a metallofullerene or endofullerene. In principle, many different atomic species can be inserted within fullerenes. An endohedrally doped fullerene molecule has modified electronic and mechanical properties. This in turn modifies the properties of the solid formed with these molecules. Therefore one can mimic electronic and mechanical properties with different number and type of dopants. As the novel form of fullerene-based material, endohedral fullerenes represents a novel type of nanostructures, which are characterized by a robust fullerene cage with atoms, ions, or clusters trapped in its hollow core. Because of the charge transfer from the encaged species to the fullerene cage, this new type of molecule has opened many possibilities for research. Metallofullerenes are characterized by many experimental techniques. EPR, via line shape and hyperfine interaction studies, provides a very sensitive method for characterizing the charge transfer for the various endohedral dopants. Other important characterization techniques for metallofullerenes include X-ray absorption fine structure, X-ray diffraction and transmission microscopy, photoelectron spectroscopy, and Mossbauer spectroscopy studies.

In present paper we have studied sodium doped C_{84} and C_{60} endohedral fullerene. Here doping is denoted by $Na@C_M$ where M=84 or 60 for one endohedral sodium atom. We have modeled the interaction between Na atoms clusters in the fullerene molecule which is assumed to be rigid. However the metal cluster inside fullerene molecule is allowed to change size. We consider that a fraction of charge is transferred from Na cluster to fullerene. The endohedral cluster $(Na)_N$ is placed such that its centre of mass coincides with the center of C_M. We have done model potential calculations to study the stability of Na clusters with various No. of atoms inside C_M. The equilibrium is obtained with minimization with charge and size of the each cluster.

2. Theoretical formalism

Fullerene molecule is considered as a spherical cage where the carbon atoms are distributed in a similar way as in the corresponding truncated icosahedrons fullerene; each carbon atom is placed on the vertices of slightly distorted pentagonal and hexagonal rings distributed on a spherical hollow cage with average radius R= 4.23Å[6]. Endohedral doping of Na atoms to fullerene molecule may result in charge transfer from Na atoms to fullerene molecule. We can expect that one or more electrons may be transferred from the Na cluster to the fullerene cage. In our calculations, the No. of atoms in the cluster varies from 1 to 9 in C_{84} and 1to 6 in C_{60} .Various interactions between Na atoms and Na and Carbon atoms of the fullerene molecule has been considered to calculate total cohesive energy of the system and hence the stability of clusters of Na atoms (cluster) inside

Full Paper

fullerene. The various components of the total cohesive energy are as under.

(i) Interaction between sodium atoms in the cluster

Let the number of Na atoms in the cluster is N. To model the metallic bonding in sodium cluster we have used the many-body Gupta potential[7], which is based on the second moment approximation of a tight-binding Hamiltonian. It uses exponential functions rather than powers of the separation. Its analytical expression is given by[8]

$$V_{GP} = V_{GP}^{REP} + V_{GP}^{ATR} = \frac{1}{2}\sum_{i=1}^{N}\left(A\sum_{i\neq j}\exp\{-p(\frac{r_{ij}}{r_0}-1)\} - \xi[\sum_{i\neq j}\exp\{-2q(\frac{r_{ij}}{r_0})-1)\}]^{\frac{1}{2}}\right) \quad (1)$$

where r_{ij} is the distance between Na atoms of the clusters and r_0, A, ξ, p and q are adjustable parameters[9]. For sodium clusters, these parameters have been fitted to band structure calculations[10]. The values are:

A = 0.01595 eV, ξ = 0.29113 eV, r_0 = 6.99 bohr, p = 10.13, q = 1.30

This potential has been already used to study the structure and thermodynamic properties of sodium clusters[11]. The Coulomb interaction between Na Atoms is given by:

$$V_{COL} = \frac{1}{2}\sum_{\substack{i,j \\ i\neq j}}^{N} K\frac{qx_i \times qx_j}{r_{ij}} \quad (2)$$

where, K is the constant, qx is the charge on each Na atom of the cluster and r_{ij} is the distance between Na atoms of the clusters. Combining Eq. 1 and 2, we have

$$V_{CLST} = V_{GP}^{REP} + V_{GP}^{ATR} + V_{COL} \quad (3)$$

(ii) Interaction between Na clusters and fullerene

Now we will consider the interaction between Na atoms with the carbon atoms of fullerene molecule. Let q be the charge transferred to fullerene molecule and M is the No. of carbon atoms . We consider that q is uniformly distributed among all carbon atoms on the fullerene molecule. Therefore the charge on each C atom is q_c = q/M. Coulomb interaction may be superimposed with van der Waals interaction used earlier in exohedral doped Na_xC_{60} compounds[10]. The resultant contribution to the energy is

$$V_{NaC84} = \frac{1}{2}\sum_{i}^{N}\sum_{j}^{M}\left[\frac{kqx_i\, q_c}{r_{ij}} + B\exp(-\alpha r_{ij})\right] \quad (4)$$

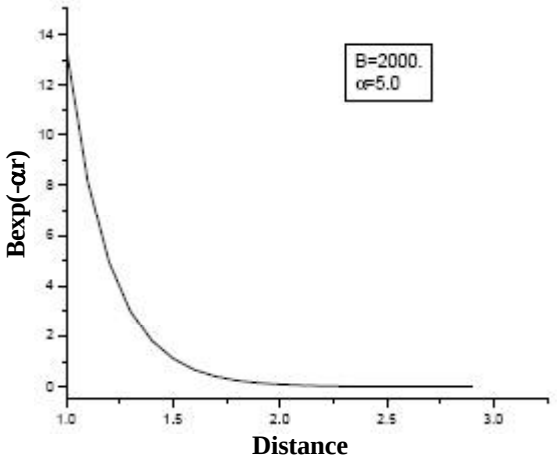

Figure 1 : Variation of repulsive potential with distance

where B=2000, α=5.0, qx =charge on each Na atom, q_c = charge on each C_M where M is 84 for C_{84} and 60 for $C_{60,}$ r_{ij} is the distance between Na atom of the clusters and C atom of C_M.

We have used figure 1 to estimate the Born-maoer parameters for sodium. Also we have adjusted V and alfa such that Na atom placed at a distance about 2Å experienced repulsion which exponentially rises for r less than 2 and therefore prevent the sodium atoms to penetrate the carbon atoms on the fullerene molecule.

The cohesive energy may be written as sum of all the contributions described above.

$$V_{COH} = V_{CLST} + V_{NaCM} \quad (5)$$

Apart from this, the electron affinity of fullerene molecule and ionization potential Na needs to be considered to discuss the stability of cluster in these systems. The electron affinity of C_{84} is 3.14 ev[12] and C_{60} is 2.65 eV[11]. Subsequent addition of electron will modify the higher electron affinity of fullerene molecule. On shell coulomb repulsion is the energy cost of placing two electrons on the same fullerene molecule. We have estimated it by adding on shell Coulomb repulsion (V) to it. The contribution to the cohesive energy is given by

$$U = -(q\times EA) + V\frac{1}{2}q(q-1) + q\times IP \quad (6)$$

where q is charge on fullerene, EA is Electron Affinity, IP ionization potential of Na and equals to 5.14 eV . Now, the total cohesive energy is obtained by adding Eqn. 5 and 6.

$$V_{TCOH} = V_{COH} + U \quad (7)$$

The Total cohesive energy V_{TCOH}, contains terms which depends upon the shape and size of the cluster of Na atoms (Eqn. 5). We can also vary the fraction of

TABLE 1 : Structure and charge on various clusters inside C_{84} and C_{60}

S. no.	No. of Na atoms	Structure of Na cluster	Charge transferred
1.	1	Single atom	1.0
2.	2	Dumbbell	2.0
3.	3	Equilateral Triangle	3.0
4.	4	Tetrahedron	4.0
5.	5	Trigonal Bipyramid	5.0
6.	6	Octahedron	6.0
7.	7	Octahedron + center	7.0
8.	8	Cube	8.0
9.	9	Cube + center	9.0

TABLE 2: Calculation results for Na doped endohedral C_{84}

No. of Na atoms	On shell coulomb repulsion	Distance of Na atom from origin	Energy E (eV)	Energy per atom E/N (eV)
	2.0	0.0	-1.1443	-1.1443
1	4.0	0.0	-1.1443	-1.1443
	6.0	0.0	-1.1443	-1.1443
	2.0	2.25	-4.425	-2.212
2	4.0	2.25	-2.425	-1.212
	6.0	2.25	-0.425	-0.212
	2.0	2.30	-7.786	-2.595
3	4.0	2.30	-1.786	-0.595
	6.0	2.30	4.214	1.404
	2.0	1.40	-11.935	-2.983
4	4.0	1.40	0.065	0.0162
	6.0	1.40	12.065	3.0162
	2.0	2.61	-11.482	-2.296
5	4.0	2.61	8.518	1.7036
	6.0	2.61	28.518	5.7036
	2.0	2.55	-24.141	-4.0235
6	4.0	2.55	5.859	0.976
	6.0	2.55	35.859	5.976
	2.0	2.70	-21.884	-3.126
7	4.0	2.70	20.116	2.873
	6.0	2.70	62.116	8.873
	2.0	1.50	-36.013	-4.501
8	4.0	1.50	19.987	2.498
	6.0	1.50	75.987	9.498
	2.0	1.60	-33.985	-3.776
9	4.0	1.60	38.015	4.223
	6.0	1.60	110.015	12.223

charge transferred to fullerene molecule. Minimization of V_{TCOH} results in equilibrium value of size of the cluster and charge on it. The fullerene molecule is assumed to be rigid.

3. RESULTS AND DISCUSSION

The structure of the metal cluster and charge transferred to fullerene molecule for different no. of Na atoms are shown in TABLE 1. TABLE 2 and figure 2 shows the variation of Total cohesive energy w.r.t V and number Na atoms inside C_{84} molecule. For each cluster, calculation has been done with different values of V. for V=2 the total cohesive energy per atom increases with increase in number of sodium atoms but not monotonically. Similar trend is seen (Figure 3 and TABLE 3 for Na doped endohedral C_{60} molecule. From figures 4-5 it is clear that total charge transfer is supported for V = 2. For V = 4 the situation is not same, the total cohesive energy is maximum for a cluster of 2 atoms inside C_{84} and then shows a gradual

TABLE 3: Calculation results for Na doped endohedral C_{60}

No. of Na atoms N	On Shell coulomb repulsion	Distance of Na atom from origin	Energy E(eV)	Energy per atom E/N(eV)
	2.0	0.0	-1.571	-1.571
1	4.0	0.0	-1.571	-1.571
	6.0	0.0	-1.571	-1.571
	2.0	1.65	-4.522	-2.261
2	4.0	1.65	-2.522	-1.261
	6.0	1.65	-0.522	-0.261
	2.0	1.84	-8.382	-2.794
3	4.0	1.84	-2.382	-0.794
	6.0	1.84	3.618	1.206
	2.0	1.15	-14.362	-3.590
4	4.0	1.15	-2.362	-0.590
	6.0	1.15	9.638	2.409
	2.0	2.20	-11.650	-2.330
5	4.0	2.20	8.350	1.67
	6.0	2.20	28.350	5.67
	2.0	2.05	-24.068	-4.011
6	4.0	2.05	5.932	0.988
	6.0	2.05	35.932	5.988

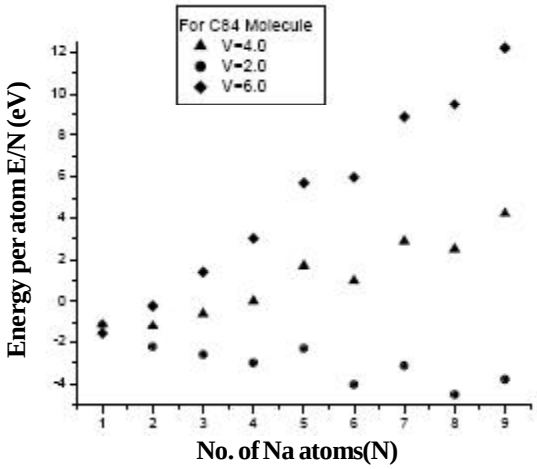

Figure 2 : Variation of energy per atom with no. of Na atoms inside C_{84}

decrease. The calculations predict unstability of a cluster composed of more than 3 atoms inside C_{84} whereas for v = 6 not more then 2 atoms will be allowed/stable inside C_{84}. Since we are not sure about the exact value of V therefore such calculations may be used to guess the value of V with observed number of Na atom clusters encapsulated inside C_{84} ,for example if more than 3 atoms of sodium can be placed inside C_{84} then it means on shell coulomb repulsion should lie between 4 and 2. The maximum distance of Na atom from the origin is 2.5 Å which is in case of 7 atom cluster. For endohedral C_{60} the calculation are presented in TABLE 3 and figure 5. Its clear energy per atom increases with increase in no. of atoms placed inside C_{60}. V=2 supports full charge transfer upto 6 atoms cluster. Again the things are interesting with V= 4 which does not support cluster formation for more than 4 atoms. Secondly, the energy per atom of N atoms cluster in C_{84} or C_{60} does not change very significantly. The size of the cluster decreases with the size of the fullerene.

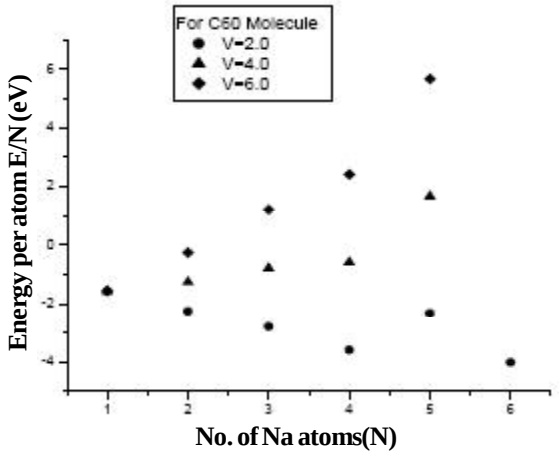

Figure 3 : Variation of energy per atom (E/N) with no. of Na atoms inside C_{60}

Apart from interactions which we have considered in our model the electron affinity and the ionization potential of metal cluster plays an important role in determining the stability of metal clusters inside a fullerene molecule. Since the higher values of electron affinity are not available in the literature therefore we have modeled it using first electron affinity and on shell coulomb

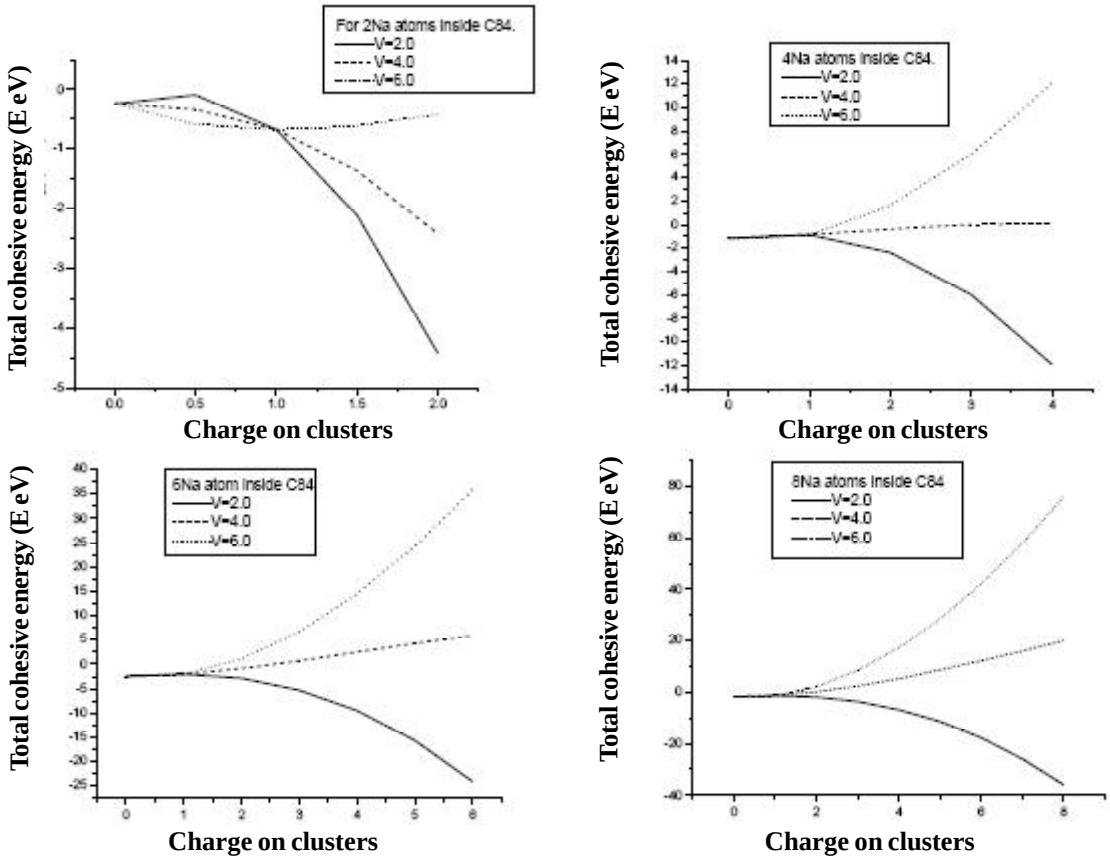

Figure 4 : (A),(B),(C) and (D)variation of total cohesive energy with charge on clusters in C_{84}

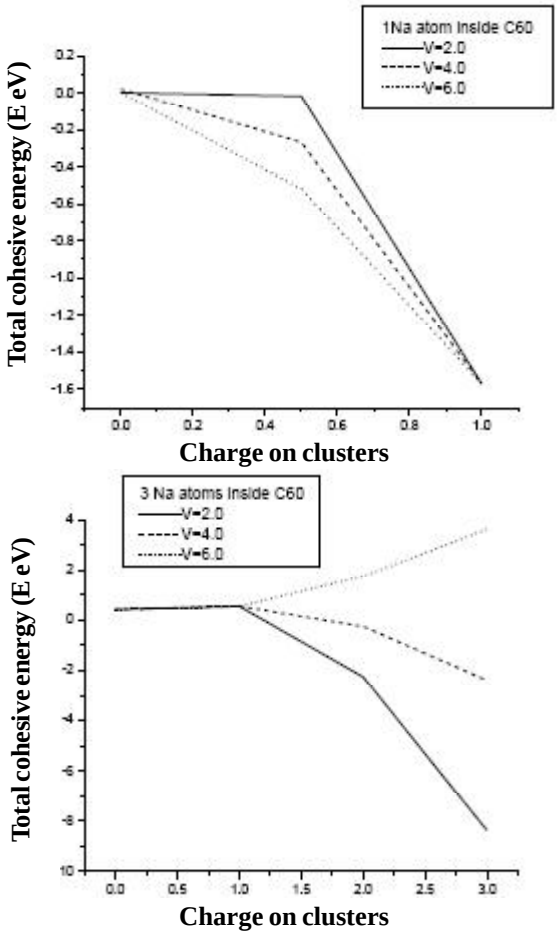

Figure 5 : (A) and (B) variation of total cohesive energy(E) with charge on clusters inside C_{60}

repulsion which solely determines the energetic/stability of the cluster inside a fullerene molecule. To see correct picture of stability of these clusters the actual higher electron affinities are very essential therefore one can go for estimation of high electron affinities.

We conclude that the cluster formation inside fullerene is supported with full charge transfer, however the value of v decides the number of atoms which can be doped inside fullerene molecule.

4. REFERENCES

[1] Laszlo Forro,Laszlo Mihaly; Rep.Prog.Phys., **64**, 649 **(2001)**.

[2] H.W.Kroto, J.R.Heath, S.C.O'Brien, R.F.Curl, R.E. Smalley; Nature, **318**, 162 **(1985)**.

[3] M.S.Dresselhaus, G.Dresselhaus, P.C.Eklund; 'Science of Fullerenes and Carbon Nanotubes', Academic Press, Inc. California, **(1996)**.

[4] L.Yarris; Carbon Cages: LBL Scientists Study Fullerenes Source: http://www.lbl.gov/Science-Articles/Archives/fullerenes.html

[5] H.O.Pierson; 'Handbook of Carbon, Graphite, Diamond and Fullerenes-Properties', Processing and Applications, Willam Andrew, **(1993)**.

[6] Amovilli; Howard, Phy.Rev., **A66**, 013210 **(2002)**.

[7] R.P.Gupta; Phys.Rev., **B23**, 6265 **(1981)**.

[8] Juan A.Reyes-Nava, Ignacio L.Garzon, Karo Michaelian; Phys.Rev., **B67**, 165401 **(2003)**.

[9] F.Cleri, V.Rosato; Phys.Rev., **B48**, 22 **(1993)**.

[10] Y.Li, E.Blaisten-Barojas, D.A.Papaconstantopoulos; Phys.Rev., **B57**, 15 519 **(1998)**.

[11] K.Ranjan, Keya Dharamvir, V.K.Jindal; Physica, **B371**, 232 **(2006)**.

[12] Compton et Al; Phys.Rev.Lett., **78**, 4367 **(1997)**.