Hexagon-preserving carbon foams: Properties of hypothetical carbon allotropes

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Carbon foams are hypothetical carbon allotropes that contain graphitelike (sp^2 carbon) segments, connected by sp^3 carbon atoms, resulting in porous structures. In this work the density-functional-based tight-binding method with periodic boundary conditions was employed to study the energetics, the stability, and the electronic properties of this unusual class of carbon systems. Concerning the most stable phases of carbon (graphite and diamond), foams show high structural stability at very low mass density. The electronic band structure and electronic density of states of foams indicate a similar size dependence as for carbon nanotubes. The calculated bulk moduli are in the range between those of graphite (5.5 GPa) and diamond (514 GPa). These structures may represent stable carbon modifications with sp^2-sp^3 hybridization. The low density and high porosity make the carbon foams interesting as materials for hydrogen storage, for example.

I. INTRODUCTION

Carbon forms several stable allotropes. At ambient conditions of pressure and temperature, the most stable crystalline carbon allotrope is hexagonal graphite, which consists of only sp^2-bonded atoms. Diamond, the second stable allotrope of carbon, is at the same conditions nearly as stable as graphite. The sp^3 carbon atoms of diamond form a very rigid three-dimensional (3D) network.

Other 3D carbon networks have been of interest for a long time. Since the discovery of fullerenes and nanotubes several other new forms of carbon have been found (onions, diamondoids, peapods) or proposed (metallic carbon $H-6$, "graphyne," scrolls). There have been numerous theoretical investigations on such new carbon forms.[1–6] This includes also the pressure-temperature phase transition of graphite into the cubic diamond structure.[7]

The focus on new carbon forms has recently emphasized structures with high stability at low mass density and big surface area. In addition to pure sp^2 or sp^3 crystals, there have been studies of mixed sp^2-sp^3 hybridized structures (isodiamond-graphite hybrids, vacancies of graphite, carbon foams,[8–11] etc.).

In the literature, there are numerous experimental works concerning carbon phases that are sp^2-sp^3 hybridized.[12–16] It was shown that some new carbon "allotropes," e.g., a superhard carbon phase produced from C_{60}, containing this mixed hybridization, appeared to have hardness higher than that of the (100) and (111) diamond faces.[12–14]

Here we study unusual systems that combine sp^2 and sp^3 hybridization of carbon atoms. Carbon foams are hypothetical carbon allotropes that contain graphitelike (sp^2 carbons) segments interconnected by sp^3 carbon atoms, resulting in porous structures.

These systems were first suggested by Karfunkel *et al.*[10] and Balaban *et al.*[8] and some of them were theoretically investigated by several authors.[11,17,18] There have been also experimental investigations with respect to the synthesis of such carbon foams.[15,16] The foam synthesis process is rather simple. The mesophase pitch precursor is molten at high temperatures resulting in so-called graphitic foams. Although these systems are not single-wall carbon foams, as are discussed in our work, they show that similar structures are achievable experimentally.

We performed systematic studies on the stability, electronic, and mechanical properties of carbon foams using the density-functional-based tight-binding (DFTB) method.[19–21] Periodic boundary conditions (PBCs) were used to represent the crystalline solid state.

The structures are constructed from graphene planes interconnected rigidly with one another at 120°, forming a linear chain of sp^3-bonded atoms along the junction. At the junctions three of the graphene layers always meet, which makes the "face" shape of the foam honeycomblike. Using different angles to connect graphene planes at the junction, one is able to construct carbon foams also with nonhexagonal cross sections. We restrict here our investigations to the foams that contain only hexagons at the junctions and have hexagonal cross sections.

Depending on the pattern of open edges, two types of such structures can be built, so called armchair or zigzag foams in analogy to the nomenclature of carbon nanotubes. The pore size is defined by two numbers $[(N,M)]$, that indicate the number of hexagonal units between the junctions. Two numbers are necessary to characterize the pore size, since one can distinguish between symmetric carbon foams of size $N=M$ and asymmetric foams with $N \neq M$. Examples of different foams are given in Fig. 1.

In comparison to the most stable phases of carbon (graphite and diamond), our calculations show high structural stability of foams at very low mass density. The electronic properties of these structures have a similar size dependence as those of zigzag and armchair carbon nanotubes. Furthermore, we found that the calculated values of the bulk moduli of carbon foams vary between those of graphite and diamond.

Carbon foams can also be considered as graphite structures with significantly increased van der Waals interlayer distance. The sp^2 carbon atoms which are transformed into sp^3 atoms make rigid interconnections between the graphite layers. The resulting highly porous and stable structures might also be interesting candidates for hydrogen storage.[22,23]
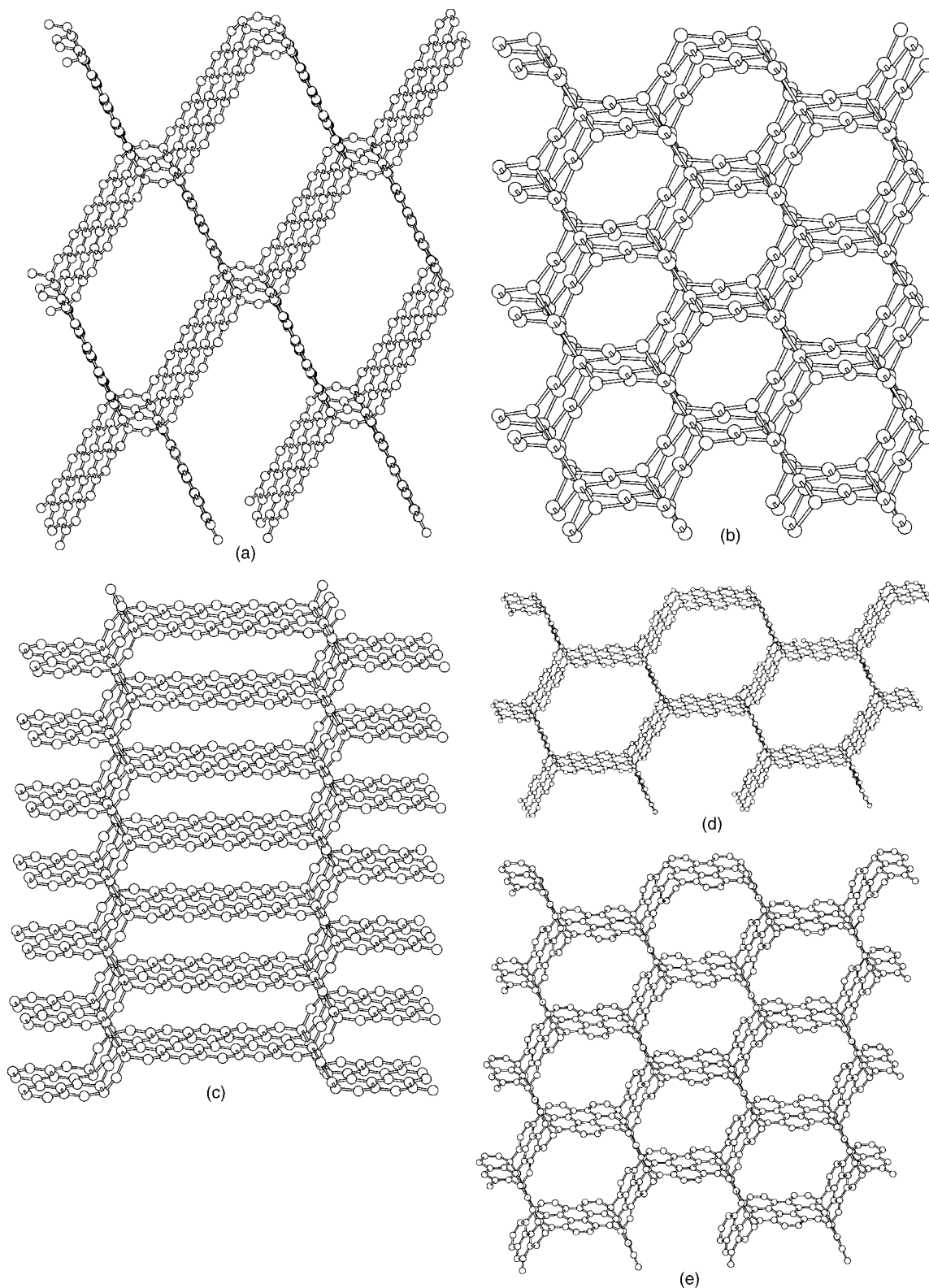
FIG. 1. Examples of carbon foam structures. (a)–(c) Zigzag carbon foams of sizes (1,5), (1,1), and (5,1), respectively; (d) and (e) armchair carbon foams (5,5) and (3,3), respectively.

II. METHODS

For the calculation of the structural and electronic properties of carbon foams, we have used the density-functional-based tight-binding method[19–21] with periodic boundary conditions. This method is a simplified density functional theory scheme, based on the linear combination of atomic orbitals representation of the Kohn-Sham wave functions.
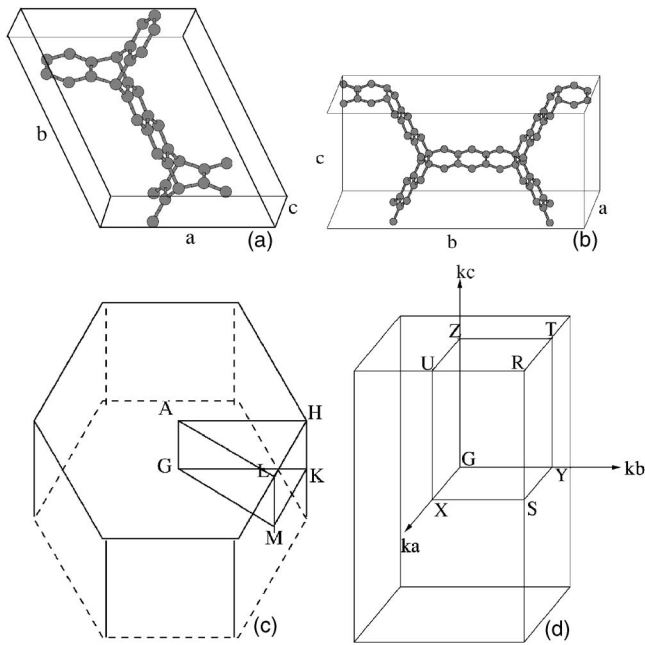
FIG. 2. The hexagonal (a) and orthorhombic (b) elementary unit cell of (3,3) zigzag carbon foam and (c), (d) the corresponding Brillouin zones.

Two-center Hamiltonian matrix elements ($h_{\mu\nu}$ are the Hamiltonian matrix elements and $S_{\mu\nu}$ the overlap matrix elements) are considered. The original version of the DFTB method in its non-self-consistent approach was used for all calculations (for more details see Refs. [19–21]).

We have calculated the band structures and densities of states using orthorhombic and hexagonal unit cells [see Figs. 2(a)–2(c)]. The choice of k points was done according to the scheme proposed by Monkhorst and Pack.[24]

The number of k points was determined by reaching convergency for the total energy, as a function of k points. We have chosen the conjugate gradient scheme for the geometry optimization. Band structures were computed along lines between high symmetry points of the Brillouin zone. The first Brillouin zones with highly symmetric points for hexagonal and orthorhombic unit cells are shown in Figs. 2(c) and 2(d).

Mechanical stability was calculated according to the symmetry of the crystal and the necessary elastic constants (stiffnesses) of the structures were computed by determining the total energy change after application of suitable strains. The coefficients of stiffnesses were further used to calculate the bulk moduli (B) of the systems.

III. RESULTS AND DISCUSSION

A. Structure

In this section we examine the geometry of carbon foams of various sizes and types. In Figs. 3(a) and 4(a), perspective views of the structures of the (3,3) zigzag and the (3,5) armchair carbon foams, are given, in comparison to the (10,0) zigzag and (5,5) armchair carbon nanotubes in Figs. 3(b), 3(d), 4(b), and 4(d) as examples. Only three hexagonal units in the a direction and two unit cells in the b and c direction
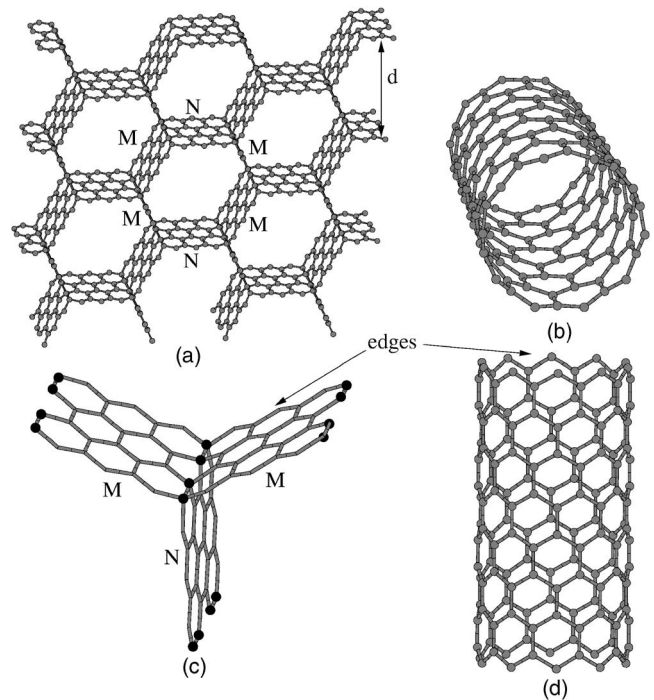

FIG. 3. Zigzag (3,3) carbon foam structure (a) and the junction (c) in comparison to the zigzag carbon nanotube (10,0) (b), (d). Foams are built using *AA* stacking of graphite planes.

are shown for visual clarity. The bonding configurations near the junctions are shown in Figs. 3(c) and 4(c) for zigzag and armchair systems. The black circles represent the linear chain of sp^3-hybridized carbon atoms at the junction through
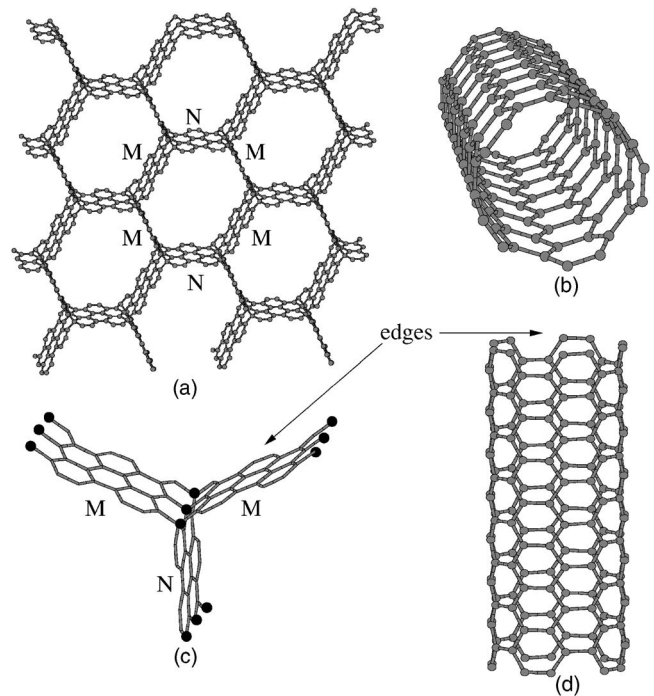

FIG. 4. Armchair (3,5) carbon foam structure (a) and the junction (c) in comparison to the armchair carbon nanotube (5,5) (b), (d). Foams are built using *AA* stacking of graphite planes.

TABLE I. The geometric parameters for symmetric zigzag and armchair carbon foams (values in brackets) compared with the calculated and experimental (values in parentheses) data for graphite and diamond.

Structure	Bond (spec.)	Bond length (Å)	Angle (spec.)	Angle value (deg)
Graphite	C-C (sp^2-sp^2)	1.420 (1.421)	C-C-C (sp^2-sp^2-sp^2)	120.11 (120.00)
Diamond	C-C (sp^3-sp^3)	1.541 (1.545)	C-C-C (sp^3-sp^3-sp^3)	109.47 (109.47)
(1,1)	C-C (sp^2-sp^2)	1.359	C-C-C	113.78
	C-C (sp^2-sp^3)	1.536	C-sp^2-C	120.00
	C-C (sp^3-sp^3)	1.557	C-sp^3-C	109.11
(2,2)	C-C (sp^2-sp^2)	1.418 [1.352, 1.448]	C-C-C	116.67 [116.41]
	C-C (sp^2-sp^3)	1.534 [1.523]	C-sp^2-C	120.00 [120.87]
	C-C (sp^3-sp^3)	1.585	C-sp^3-C	109.16 [110.46]
(3,3)	C-C (sp^2-sp^2)	1.420 [1.372, 1.442]	C-C-C	117.72 [117.46]
	C-C (sp^2-sp^3)	1.530 [1.518]	C-sp^2-C	120.00 [120.63]
	C-C (sp^3-sp^3)	1.567	C-sp^3-C	109.17 [110.07]
(4,4)	C-C (sp^2-sp^2)	1.424 [1.384, 1.436]	C-C-C	118.26 [117.83]
	C-C (sp^2-sp^3)	1.531 [1.515]	C-sp^2-C	120.00 [120.41]
	C-C (sp^3-sp^3)	1.576	C-sp^3-C	109.16 [109.23]
(5,5)	C-C (sp^2-sp^2)	1.425 [1.394, 1.443]	C-C-C	118.60 [118.12]
	C-C (sp^2-sp^3)	1.532 [1.515]	C-sp^2-C	120.00 [120.27]
	C-C (sp^3-sp^3)	1.575	C-sp^3-C	109.17 [108.81]

the foam in the a direction. According to our calculations the bonds at the junctions are only slightly distorted from the ideal tetrahedral bonds of diamond.

All possibilities for N, $M=1-5$ were investigated. In addition, two larger structures of the armchair type were calculated: (7,7) and (9,9).

The elementary unit cells of zigzag and armchair carbon foams differ from each other in the number of atoms (n) for a given pore size. As an example, the (2,2) carbon foam consists of 44 and 20 carbon atoms for a zigzag and for an armchair foam, respectively.

All structures can be represented in orthorhombic 3D carbon networks. Moreover, the zigzag foams with $N=M$ can be described within a hexagonal lattice as well.

The interlayer distances d [see Figs. 3(a) and 4(a)] vary in the range of 4.7–32.3 Å. The orthorhombic unit cell in the a direction can be as short as 2.465 and 4.269 Å for the armchair and zigzag carbon foams, respectively.

The pore size is determined by the b and c parameters of the unit cell. Keeping a at its minimum and reducing the width in the b and c directions to zero ($N,M=0$), the structure reduces to a network of fourfold-coordinated carbon atoms, namely, that of cubic diamond (armchair carbon foams) or hexagonal diamond (isodiamond; zigzag carbon foams).[8,25] On the other hand, increasing the a and b parameters gives in the $a,b\rightarrow\infty$ limit the structure of an isolated single graphene layer.

The structures of zigzag and armchair systems are different also in the types of connections (bonds): three types of covalent bonds sp^2-sp^2, sp^2-sp^3, and sp^3-sp^3 can be found for the zigzag arrangement, while in armchair foams there are two kinds of sp^2-sp^2, bonds (single and double; see Table I, values given in parentheses) and sp^2-sp^3 (no sp^3-sp^3, di-

rect connections along the a direction at the junction). Comparing the geometries of carbon foams with the corresponding data for graphite and diamond (see Table I), one can see that the bond lengths are between the values for the two carbon allotropes. Only the sp^3-sp^3, bonds are slightly larger than that for diamond. Moreover, the angles at the threefold- and fourfold-coordinated atoms are the same as those in graphite and diamond, respectively.

The C–C (sp^2-sp^2) bond lengths in the zigzag foams are very close to the bond lengths in graphite, whereas in armchair foams single and double bonds between sp^2 carbon atoms exist. The difference between single and double bonds decreases with increasing size, approaching the value of graphite.

Furthermore, the results indicate that the optimized unit cell sizes of carbon foams correspond to mass densities smaller than that of graphite ($\rho=2.27$ g/cm^3) and diamond ($\rho=3.54$ g/cm^3)—see Fig. 5. The only system with a slightly bigger value than that of graphite is the (1,1) zigzag foam with a mass density of $\rho=2.42$ g/cm^3.

The smallest armchair foams $(N,1)$, with an initial distance between the graphitic segments smaller than the van der Waals interlayer distance of graphite, become very interesting systems after full geometry optimization—see Fig. 6. The sp^3 atoms of those structures open one of the four bonds and bind strongly only to three neighbors, resulting in a porous system, built only from sp^2 carbon atoms (we will call them "sp^2 carbon foams"). As an example the (3,1) armchair foam is shown in Fig. 6(a). The distance d of 3.239 Å between the graphitic fragments, as well as the bond lengths, of this structure are similar to those of layered graphite, while the arrangement of atoms is different. This carbon foam has a mass density of $\rho=2.47$ g/cm^3, only slightly larger than
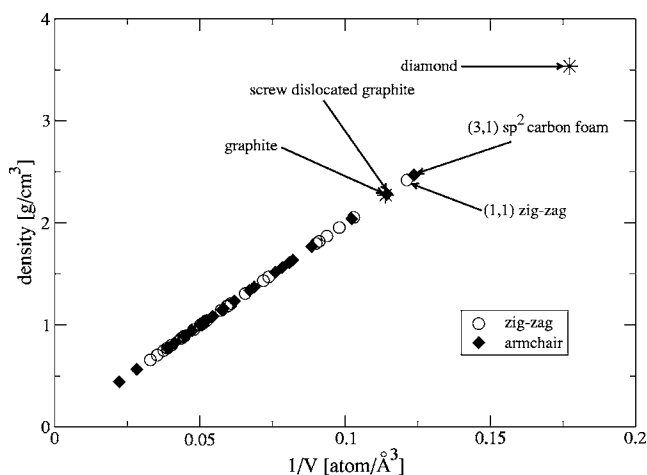
FIG. 5. The mass density of carbon foams versus $1/V$ (V is the atomic volume in units of $\text{Å}^3/\text{atom}$), compared to graphite and diamond.

that of layered graphite. Analogous sp^2 foams were also discussed by Umemoto *et al.*[11]

Similar foam structures can be constructed by screw twisting of graphite layers. These might be related to the structure of screw dislocated graphite[26] (SDG); see Fig. 6(b). Therefore, we call here this type of carbon foam "screw dislocated graphite." It has the same interlayer distance (d) and bond lengths as layered graphite; however, there appear also bonds in the c direction that connect the ab planes. By construction, these bonds are formed by providing atoms within the graphene layers with additional neighbors in the c direction, locally removing planarity without changing the hybridization of carbon atoms. The system—shown in Fig. 6(b)— corresponds to a (7,1) armchair carbon foam.

Both types of sp^2 foams have different kinds of nanopores that form 3D interconnected channels: sp^2 foams have direct connections between pores when looking along the b direction [Fig. 6(a), bottom], while SDG connections are rather twisted [Fig. 6(b), bottom]. On the other hand, the sp^2-sp^3 carbon foams have closed nanopores (tubes), similar to nanotubes.

B. Energetic considerations and mechanical stability

Carbon foams are hypothetical forms of carbon, however, interesting results where found from experimental and theoretical investigations. The experiment of Wang *et al.*,[27] where a sample of carbon nanotubes was cold compressed in a diamond anvil cell, shows transformation into what is believed to be a possible novel carbon allotrope. The recent results of theoretical work of Bucknum *et al.*[28] show that the new form of carbon obtained by Wang *et al.* can be described by carbon foams. The results indicate that possibly kinetically stabilized products, such as low-density carbon-foam-like materials, may have been formed. It was also shown that a new crystalline carbon phase is a hard phase of carbon with a high (calculated) value of bulk modulus.[28]

We have calculated the stability and energetics of carbon foams in general to describe the energetic and mechanical properties of those systems.
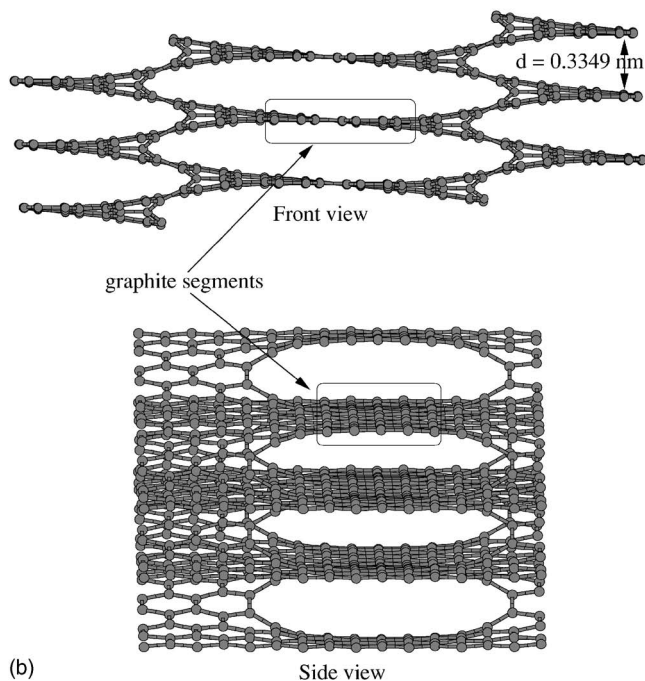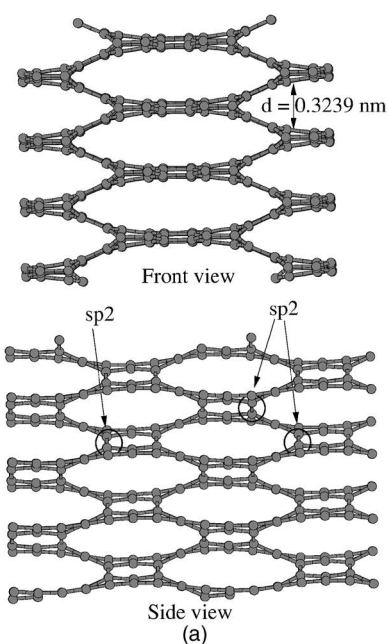

FIG. 6. The structure (sp^2) of the (3,1) armchair carbon foam (a) and screw dislocated graphite (b). Both are obtained from the AA stacking of graphite layers.

The binding energy (per atom) as a function of n (n is the number of atoms in the unit cell) is shown in Fig. 7.

The total number of atoms n in the elementary cell consists of carbon atoms at the boundaries (junctions), n_x, and the atoms inside the graphene fragments (stripes), n_i. The energy of such carbon foams can be written as

$$E_{bind} = n_i \epsilon_\infty + n_x \epsilon_x. \qquad (1)$$

ϵ_∞ is the binding energy per atom of the infinite graphite monolayer, whereas ϵ_x describes the binding energy of the
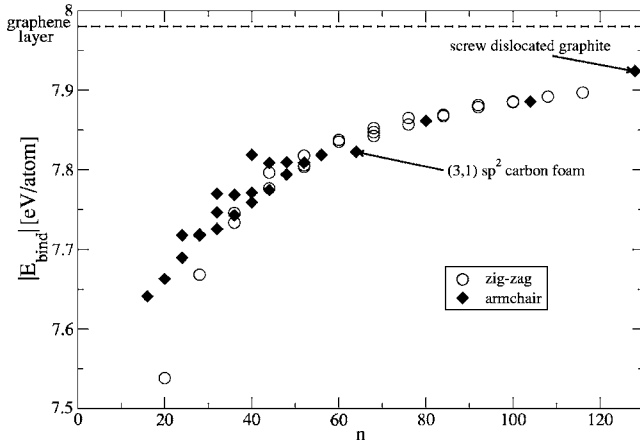
FIG. 7. The binding energy of carbon foams as a function of the number of atoms n per unit cell. The corresponding energy of a single graphene layer is given as a reference.

boundary atoms. Since $n=n_i+n_x$, the energy may be written as follows;

$$E_{bind} = n\epsilon_\infty - n_x\epsilon_\infty + n_x\epsilon_x. \qquad (2)$$

Defining $\Delta\epsilon = \epsilon_x - \epsilon_\infty$, the energy per atom becomes

$$\frac{E_{bind}}{n} = \epsilon_\infty + \frac{n_x\Delta\epsilon}{n}. \qquad (3)$$

The number n_x of boundary atoms per unit cell is constant, $n_x=8$.

Figure 8 shows that the energy of carbon foams increases nearly linearly as $1/n$ with increasing size, as expected from Eq. (3), asymptotically approaching the binding energy of a graphene monolayer. The deviations from linearity (see Fig. 8) may be explained as the differences in the types of boundary atoms (n_x) for a given kind of structure. In zigzag systems there are eight sp^3 carbon atoms per elementary unit cell, while four sp^2 and four sp^3 carbon atoms (per unit cell) occur at the junctions in armchair structures (see Fig. 9). The sp^2 carbon atoms in zigzag foams form graphene stripes with
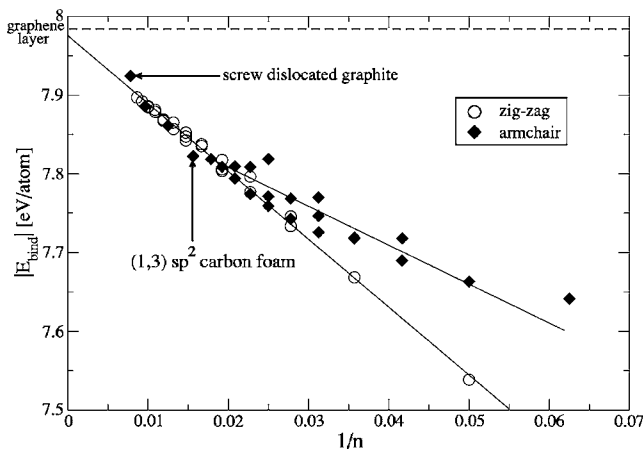

FIG. 8. The binding energy as a function of $1/n$ (n is the number of atoms per unit cell). For comparison the corresponding energy of a graphene monolayer is given as reference.
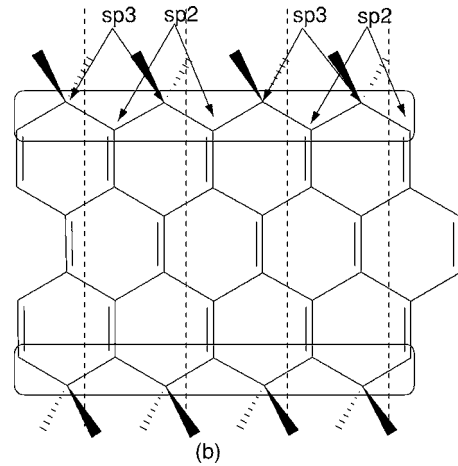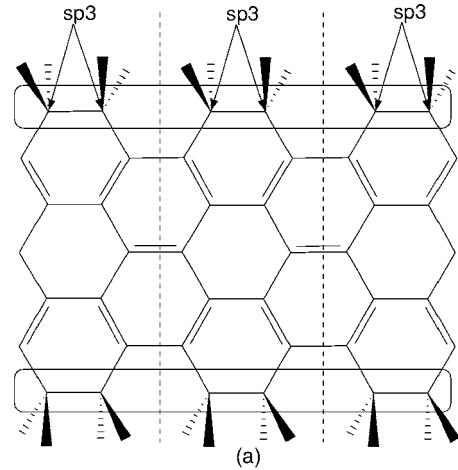

FIG. 9. The atoms at boundaries in zigzag (a) and armchair (b) carbon foams. The unit cells are indicated by dashed lines.

a fully delocalized π-electron system, whereas the π-electron delocalization is distorted by the π bonds to the sp^2 atoms at the boundary of graphenelike stripes in armchair foams. This has obviously a stronger influence in smaller structures. For larger systems the bonding behavior of all boundary atoms becomes very similar, i.e., all structures have nearly the same $1/n$ size dependence. This is also confirmed by the tendency of sp^2-sp^2 bond lengths in armchair systems. With increasing size the values of single and double bonds become closer to each other, and similar to the size in zigzag systems (see Table I).

Our calculations indicate that carbon foams are quite stable systems when compared to the well-known carbon allotropes. The origin of their favorable stability is the fact that the carbon foams discussed here do not contain bent but only strained graphitic planes, in contrast to the fullerens and nanotubes which are purely sp^2 bonded. The biggest (5,5) zigzag carbon foam ($n=116$) is almost as stable as graphite and diamond. We find its cohesive energy to be smaller by only ~ 0.09eV/atom than that of graphite ($E_{bind}=7.986$ eV/atom). The least stable (1,1) zigzag carbon foam ($n=20$) with energy of 7.538 eV/atom is as stable as a (5,5) armchair carbon nanotube ($E_{bind}=7.539$ eV/atom) and similarly stable as a (10,0) carbon nanotube. The results show

TABLE II. The bulk B (left) and the shear G (right) moduli for zigzag carbon foams in GPa.

						M				
		B					G			
N	1	2	3	4	5	1	2	3	4	5
1	285.1	89.0	21.5	8.25	4.25	176.95	53.1	15.3	4.3	3.6
2	265.5	157.7	54.85	18.3	6.95	105.8	32.3	13.5	6.6	3.2
3	225.2	172.9	97.0	69.5	21.0	122.7	17.9	8.7	8.1	4.6
4	148.6	137.3	124.8	73.9	69.1	142.8	11.6	6.3	4.6	4.6
5	183.5	107.9	109.4	98.9	75.5	76.5	7.95	5.0	3.8	2.9

that, except for the (1,1) zigzag carbon foam, all structures are more stable than nanotubes and the isolated C_{60} cage (E_{bind}=7.569 eV/atom) by at least ~0.08 eV/atom.

Moreover, the sp^2 carbon foams are very stable as well. As an example, the (3,1) foam is less stable by ~0.16 eV/atom than graphite and diamond. The structure of the SDG with energy of 7.924 eV/atom is similarly stable to the most stable carbon allotropes. These results suggest that carbon foams are stable once they are formed.

The mechanical properties were studied by estimation of the bulk moduli using the finite-difference scheme (the derivatives of the total energy with strains $\epsilon_{i,j}$). The elastic constants (stiffness) c_{ij} were calculated using the finite-difference scheme (the derivatives of the total energy with respect to strains $\epsilon_{i,j}$) as in Eq. (4):

$$\frac{\partial}{\partial \epsilon_j}\left(\frac{\partial E}{\partial \epsilon_j}\right) = c_{ij}. \qquad (4)$$

The matrix of constants was further used to obtain the bulk modulus as follows:

$$B = \frac{1}{9}[c_{11} + c_{22} + c_{33} + 2(c_{12} + c_{13} + c_{23})] \qquad (5)$$

for the orthorhombic lattice or

$$B = \frac{\Delta c_{33} + 2c_{13}}{\Delta + 2}, \qquad (6)$$

where

$$\Delta = \frac{c_{11} + c_{12} - 2c_{13}}{c_{33} - c_{13}}, \qquad (7)$$

for the hexagonal one. The shear modulus (G) can be calculated according to Eq. (8):

$$G = \frac{1}{15}[(c_{11} + c_{22} + c_{33} - c_{12} - c_{13} - c_{23}) + 3(c_{44} + c_{55} + c_{66})]. \qquad (8)$$

The results (see Tables II and III) show that on increasing the size (N,M), of carbon foams the value of the bulk modulus decreases; however the smallest belongs to the (1,5) zigzag foam (4.25 GPa). The shear modulus decreases also with increasing size of the foam and the smallest was found for the (7,7) armchair system.

The stiffest carbon foam is the (1,1) zigzag with a bulk modulus of 285.13 GPa and a shear modulus of 176.95 GPa. It is interesting to note that the armchair carbon foams seem to be more stable mechanically than zigzag structures for a given pore size. The other tendency obtained is that the bulk and the shear moduli become smaller when going from systems with $M=1$ to 5.

As expected for structures built from graphite and diamond segments with mixed sp^2-sp^3 hybridization, the calculated values of bulk moduli of carbon foams vary over a wide range: ~5 up to ~300 GPa, i.e., ranging from the value of graphite (5.5 GPa) almost to that of diamond (514 GPa). Moreover, the sp^2 carbon foams, the (3,1) armchair and SDG, possess rather large bulk moduli of 48.5 and 20.2 GPa, respectively, in comparison to graphite. On the other hand, the G values for carbon foams are clearly smaller than those of diamond (621 GPa) and for bigger structures they become close to that of graphite (3 GPa).

Evidently the carbon foams are mechanically rather stable concerning the bulk moduli. However, larger foams (see Tables. II and III) could become unstable against shear forces.

TABLE III. The bulk B (left) and the shear G (right) moduli for armchair carbon foams in GPa.

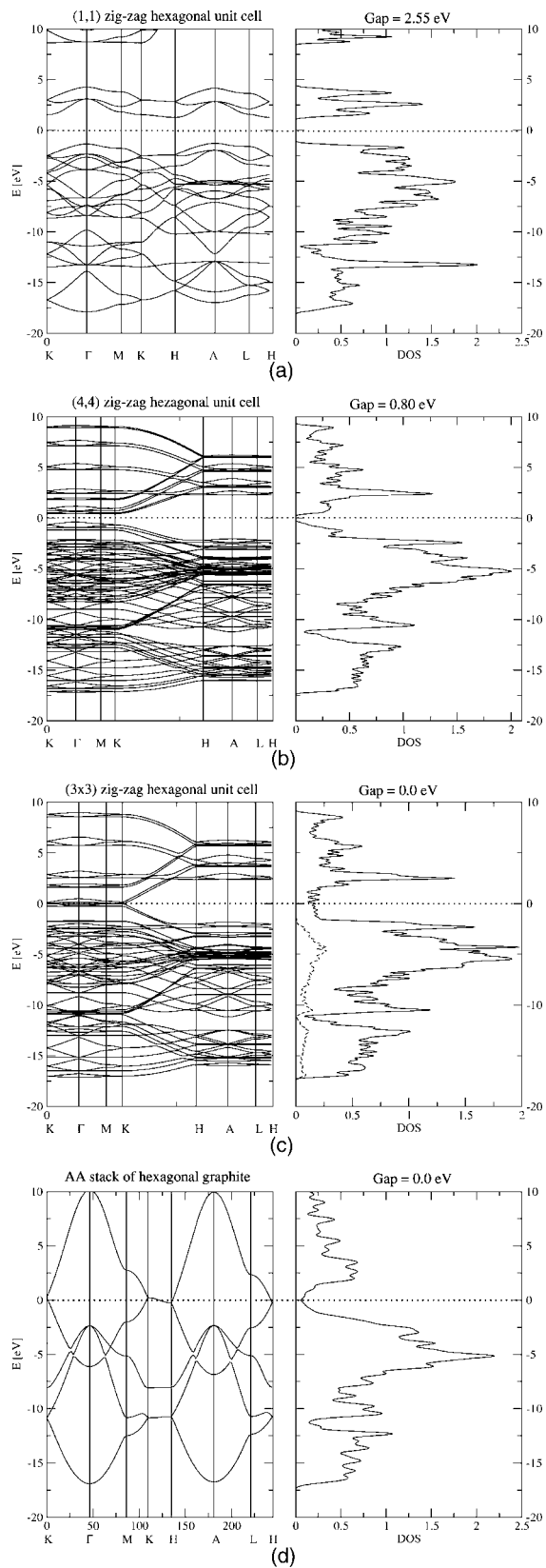|						M						
			B						G			
N	2	3	4	5	7	9	2	3	4	5	7	9
1	266.7	78.2	28.8	12.6			64.35	24.65	12.45	7.9		
2	213.3	156.3	57.4	23.4			26.2	16.8	9.2	6.4		
3	140.6	162.1	95.7	47.2			12.2	8.7	4.7	4.3		
4	89.6	114.8					9.0	4.3				
5	65.0	88.2	100.6	92.3			3.6	3.7	2.4	0.9		
7					65.9						0.1	
9						32.6						

FIG. 10. The band structures and the DOSs of some symmetric zigzag carbon foams (a)–(c) and graphite (d); hexagonal lattice representation; Fermi level shifted to 0.0 eV. The DOS is given in units of states/hartree atom. The dashed line in (c) denotes the partial DOS of sp^3 carbon atoms along the "junction line."
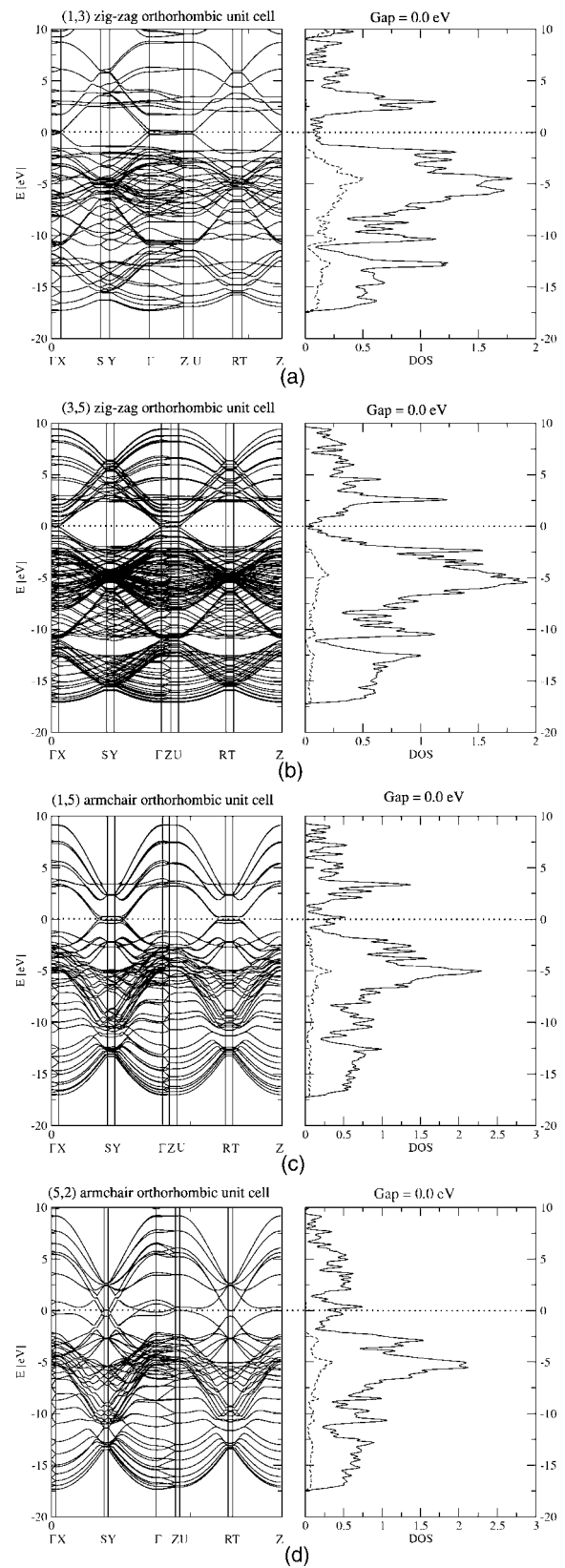
FIG. 11. The band structures and the corresponding DOSs of some orthorhombic zigzag (a), (b) and armchair (c), (d) carbon foams; Fermi level shifted to 0.0 eV. DOS is given in units of states/hartree atom. The dashed line in (c) denotes the partial DOS of sp^3 carbon atoms along the "junction line."
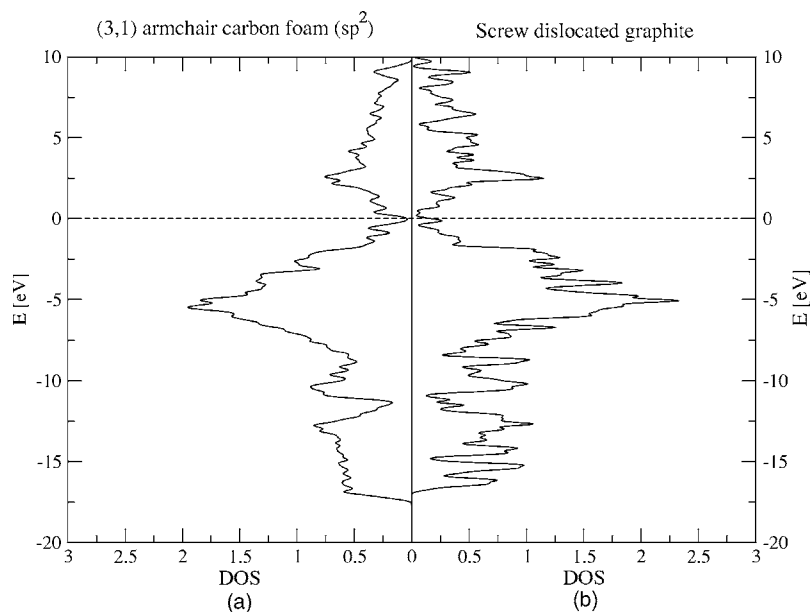
FIG. 12. DOSs of the (3,1) armchair carbon foam (left) and the screw dislocated graphite (right); Fermi level shifted to 0.0 eV. DOS is given in units of states/hartree atom.

C. Electronic structure

In this section the electronic properties (densities of states and band structures) of carbon foams are discussed. The calculated band gaps of zigzag foams have a similar size dependence as those of zigzag nanotubes. They are metallic, if the distance between two junctions is a multiple of three hexagonal units:

$$(N,M) = [3m,M] \qquad (9)$$

and/or

$$(N,M) = [N,3m], \qquad (10)$$

with $m = 1, 2, 3, \ldots$; otherwise the foams are semiconducting. On the other hand, the armchair carbon foams are metallic, independent of size, similar to armchair carbon nanotubes.

Figure 10 shows the band structures and densities of states (DOSs) for the symmetric zigzag carbon foams calculated on a hexagonal lattice. These results are compared with the band structure and DOS of hexagonal graphite.

The gap size for most of the semiconducting structures is in the range of those for semiconducting carbon nanotubes (0.6–1 eV), except for the (1,1) zigzag carbon foam. Although the dispersion along the lowest conduction band as well as of the highest valence band is very small, the systems may be considered as indirect gap semiconductors. This can make foams interesting concerning possible applications utilizing the optical properties. A distinct dispersion appears along the KH lines. Our calculations of electronic structure reveal that mostly the atoms in the direct neighborhood of the sp^3 C atom chain contribute to the bands near the Fermi level. The (3,3) zigzag carbon foam is metallic with the bands crossing the Fermi level at the K point of the Brillouin zone.

Some examples of band structures and DOSs of the orthorhombic ($N \neq M$) zigzag carbon foams are shown in Figs. 11(a) and 11(b). They are metallic with a large band disper-

sion in the k_a-k_b plane, similar to that of a graphene monolayer.

Electronic properties of some armchair carbon foams are shown in Figs. 11(c) and 11(d). This group of metallic structures has bands crossing the Fermi level along the XS and $Y\Gamma$ lines. A large dispersion of valence and conduction bands is visible.

In Figs. 10 and 11 we show for the metallic systems also the partial DOS of the sp^3 carbon atoms. It can be seen that the line of junction atoms have insulating character and the metallic properties of the carbon foam are restricted to graphenelike stripes with sp^2-hybridized carbon atoms.

The family of sp^2 armchair foams is also metallic. The densities of states of the (3,1) structure and the SDG are shown in Fig. 12. The band structures are very complicated (not shown here).

IV. CONCLUSIONS

In this work hypothetical carbon allotropes, called carbon foams, have been discussed with reference to their stability and electronic properties. The geometry optimization of these structures was performed using the DFTB method within PBCs. The construction shows that the chain of sp^3-hybridized atoms along the junction is connected covalently with layers of graphite stripes having either zigzag or armchair types of edges.

The results indicate carbon foams to be stable, when related to the most stable carbon phases (graphite and diamond), and structurally quite rigid. These systems may represent porous carbon modifications with sp^2-sp^3 hybridization and high structural stability at low mass density. Moreover, this family of 3D network carbon structures has large bulk moduli; however, with increasing size of the foams they may become unstable against shear forces.

Their electronic properties can be related to those of carbon nanotubes: all armchair foams are metallic, and those zigzag structures with distances between junctions that are

multiples of three hexagonal units are metallic as well; otherwise they are semiconducting. The metallic character is due to graphenelike stripes, while the sp^3 chains at the junctions are insulating.

There have been found also other very stable metallic carbon foams consisting only of sp^2 atoms with similar mechanical and energetic properties.

The high porosity and accessibility of the foam structures suggest their great potential for the storage of hydrogen.

The investigations on carbon foams are still in progress but the results should encourage experimental investigations for the synthesis of such new carbon systems.

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[1] D. Tomanek, Physica B **323**, 86 (2002).

[2] A. Y. Liu and M. L. Cohen, Phys. Rev. B **45**, 4579 (1992).

[3] A. Y. Liu, M. L. Cohen, K. C. Hass, and M. A. Tamor, Phys. Rev. B **43**, 6742 (1991).

[4] C. Mailhiot and A. K. McMahan, Phys. Rev. B **44**, 11578 (1991).

[5] G. C. McIntosh, M. Yoon, S. Berber, and D. Tomanek, Phys. Rev. B **70**, 045401 (2004).

[6] R. Hoffmann, T. Hughbanks, M. Kertesz, and P. H. Bird, J. Am. Chem. Soc. **105**, 4831 (1983).

[7] F. J. Ribeiro, S. G. Louie, M. L. Cohen, and P. Tangney, Phys. Rev. B **72**, 214109 (2005).

[8] A. T. Balaban, D. J. Klein, and C. A. Folden, Chem. Phys. Lett. **217**, 266 (1994).

[9] R. H. Telling, C. P. Ewels, A. A. El-Barbary, and M. I. Heggie, Nat. Mater. **2**, 333 (2003).

[10] H. R. Karfunkel and T. Dressler, J. Am. Chem. Soc. **114**, 2285 (1992).

[11] K. Umemoto, S. Saito, S. Berber, and D. Tomanek, Phys. Rev. B **64**, 193409 (2001).

[12] V. D. Blank, S. G. Buga, N. R. Serebryanaya, V. N. Denisov, G. A. Dubitsky, A. N. Ivlev, B. N. Mavrin, and M. Y. Popov, Phys. Lett. A **205**, 208 (1995).

[13] N. R. Serebryanaya, V. D. Blank, V. A. Ivdenko, and L. A. Chernozatonskii, Solid State Commun. **118**, 183 (2001).

[14] A. V. Talyzin, L. S. Dubrovinsky, M. Oden, T. Le Bihan, and U. Jansson, Phys. Rev. B **66**, 165409 (2002).

[15] J. W. Klett, A. D. McMillan, N. C. Gallego, and C. A. Walls, J. Mater. Sci. **39**, 3659 (2004).

[16] J. Klett, R. Hardy, E. Romine, C. Walls, and T. Burchell, Carbon **38**, 953 (2000).

[17] N. Park and J. Ihm, Phys. Rev. B **62**, 7614 (2000).

[18] J. A. Van Vechten and D. A. Keszler, Phys. Rev. B **36**, 4570 (1987).

[19] G. Seifert, D. Porezag, and T. Frauenheim, Int. J. Quantum Chem. **58**, 185 (1996).

[20] T. Frauenheim, G. Seifert, M. Elstner, Z. Hajnal, G. Jungnickel, D. Porezag, S. Suhai, and R. Scholz, Phys. Status Solidi B **217**, 41 (2000).

[21] T. Frauenheim, G. Seifert, M. Elstner, T. Niehaus, C. Kohler, M. Amkreutz, M. Sternberg, Z. Hajnal, A. Di Carlo, and S. Suhai, J. Phys.: Condens. Matter **14**, 3015 (2002).

[22] L. Zhechkov, T. Heine, S. Patchkovskii, G. Seifert, and H. A. Duarte, J. Chem. Theory Comput. **1**, 841 (2005).

[23] S. Patchkovskii, J. S. Tse, S. N. Yurchenko, L. Zhechkov, T. Heine, and G. Seifert, Proc. Natl. Acad. Sci. U.S.A. **102**, 10439 (2005).

[24] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[25] C. X. Wang, Y. H. Yang, Q. X. Liu, G. W. Yang, Y. L. Mao, and X. H. Yan, Appl. Phys. Lett. **84**, 1471 (2004).

[26] I. Suarez-Martinez, G. Savini, and M. I. Heggie, in Proceedings of the Conference Carbon 2006, Aberdeen (unpublished).

[27] Z. W. Wang, Y. S. Zhao, K. Tait, X. Z. Liao, D. Schiferl, C. S. Zha, R. T. Downs, J. Qian, Y. T. Zhu, and T. D. Shen, Proc. Natl. Acad. Sci. U.S.A. **101**, 13699 (2004).

[28] M. J. Bucknum and E. A. Castro, J. Chem. Theory Comput. **2**, 775 (2006).