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First-principles study of graphite monofluoride $(CF)_n$

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The structure and the electronic properties of graphite monofluoride $(CF)_n$ have been studied within the framework of the density-functional technique, using nonlocal ionic pseudopotentials and a large number of plane waves. The chair conformation is shown to be energetically favored with respect to the boat conformation by 0.145 eV per CF unit. The transition between these two states has been investigated: the boat conformation is metastable, with an estimation of the transition barrier on the order of 2.72 eV. This indicates that the material actually synthesized could depend on the kinetics of the intercalation or could as well be a mixing of both conformations. The equilibrium geometries are compared with experimental data. We also present the valence charge density and the band structure of the chair conformation.

I. INTRODUCTION

Although discovered long ago,[1] the phenomenon of intercalation has only been thoroughly studied for 40 years. It is defined as the insertion of atoms into the interplanar voids of a lamellar structure without destruction of the host's layered bonding network.[2] Graphite, which presents a lamellar hexagonal lattice, is a peculiar material for this phenomenon. The graphite sheets may be viewed as huge aromatic macromolecules in which bonding between carbon atoms involves sp^2 hybridized orbitals.[3] The remaining electron per carbon atom enters a delocalized orbital of p-π symmetry, which can give rise to a bond with a reactant atom upon intercalation.

Fluorination of graphite leads[4,5] to the production of polycarbon monofluoride $(CF)_n$, commonly known as graphite monofluoride, one of the most stable polymeric fluorocarbons, an exceptional lubricant[6] under the extreme conditions of high temperature and high vacuum, and a quite successful cathodic depolarizer in a high-energy density battery.[7] Its structure, which is layered, is derived from graphite by insertion of covalently bonded fluorine atoms *above* and *below* every hexagon in each layer. By forming these covalent bonds to the carbon atoms (s^2p^2), fluorine atoms (s^2p^5) disrupt the aromatic network and generate nonconducting graphite derivatives in which single carbon sheets are buckled rather than planar. Many of its unique properties arise from the lamellar structure of weakly coupled sp^3 carbon-fluorine sheets. On the other hand, the production at ambient temperature of "carbon-fluorine compounds" (C_xF) in the presence of acidic fluoride maintains the flat carbon layer after fluorine intercalation due to the ionic or semi-ionic character of the C-F bond imposed by the preparation method.[8]

The determination of the structure of $(CF)_n$ has presented great difficulties[9] from the earliest work up to now, due in great part to the problems encountered in growing single crystals. Some doubt still persists in the way these carbon layers are puckered. The Rüdorff structure,[4] proposed in the early state of the discovery, is an infinite array of *trans*-linked cyclohexane chairs [Fig. 1(a)], while one other possible conformation is an infinite array of *cis-trans*-linked cyclohexane boats[10] [Fig. 1(b)]. X-ray powder-diffraction studies[10,11] are in agreement with the chair structure, indicating an hexagonal crystal lattice, while NMR second moment measurements[12] favor the boat structure, which results in an orthorhombic crystal lattice. These two conformations are covalent compounds containing tetrahedrally coordinated sp^3 hybridized carbon atoms.

The aim of this study is to investigate from first principles the structure and the stability of these two conformations of graphite monofluoride, and to study more closely the electronic properties of the most stable one. In Sec. II, we start with a critical discussion of the *ab initio* theoretical method we used to study the above-mentioned properties: a self-consistent density-functional approach, using *ab initio* nonlocal pseudopotentials and a local-density approximation for exchange and correlation. The energetical study of the two conformations is presented in Sec. III. Numerical results for the electronic properties

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of the chair conformation are shown in Sec. IV. Finally, we summarize and comment on our results.

II. THEORETICAL METHOD

The density-functional theory[13] (DFT), which is an effective tool in studying the total energy and the electronic structure of solids with no parametrization to experimental data, has been implemented[14] within the local-density approximation[15] using the conjugate-gradient algorithm,[16] where diagonalization and self-consistency steps are carried out simultaneously. This method has been applied to graphite monofluoride where the atomic potentials plus core electrons of carbon and fluorine have been replaced by extended norm-conserving separable *ab initio* pseudopotentials.[17] A polynomial parametrization[18] of the exchange-correlation functional of Ceperley-Alder[19] and a kinetic-energy cutoff of 35 hartree [about 2200 plane waves (chair) and 5100 plane waves (boat)] have been used. The Brillouin-zone integration on special point grids[20] of two, four, and ten special k points (chair); two, five, and thirteen special k points (boat) have been studied in order to estimate convergence errors. The discrepancies on total energy calculation due to the finite set of special k points are, respectively, 0.013 eV/atom (four k points) in the chair conformation and 0.009 eV/atom (five k points) in the boat one. Around 35 hartree, the calculated error on the total energy due to the finiteness of the plane waves set is ± 0.04 eV/atom in both conformations. Of course, when comparing the two different structures, only the relative error in energy is important, and it can be evaluated to be 3 meV/atom due to the Brillouin-zone integration, and < 1 meV/atom due to the number of planes waves.

The structural optimization study of graphite monofluoride has been carried out starting with unperturbed graphitic planes and relaxing the structure according to the forces and stresses obtained as derivatives of the total energy, by the Hellmann-Feynman theorem and the stress theorem.[21] The different crystalline parameters have been considered accurate enough when the diagonal elements of the corresponding stress tensor were below a threshold value ($\sigma_{11}, \sigma_{22} < 10^{-6}$ hartree/bohr^3, $\sigma_{33} < 10^{-4}$ hartree/bohr^3), while the residual forces on the atoms were inferior to 10^{-5} hartree/bohr. The Pulay correction[22] has been added to the stress tensor and to the total energy to decrease the error due to the use of different sets of plane waves.

III. STRUCTURAL PROPERTIES

The structural study has been limited to the AAA stacking (each carbon atom have a corresponding atom in the plane directly above and below), which should not affect the intraplanar structure, the principal interest of this work.

The infinite array of *trans*-linked cyclohexane chairs is a layered structure, derived from graphite by insertion of three covalently bonded fluorine atoms above and three fluorine atoms below every hexagon in each layer, which then becomes puckered as shown in Fig. 1(a). The unit cell of this structure, which contains four atoms (2F+2C), is hexagonal and the space group is $P6_3mc$.

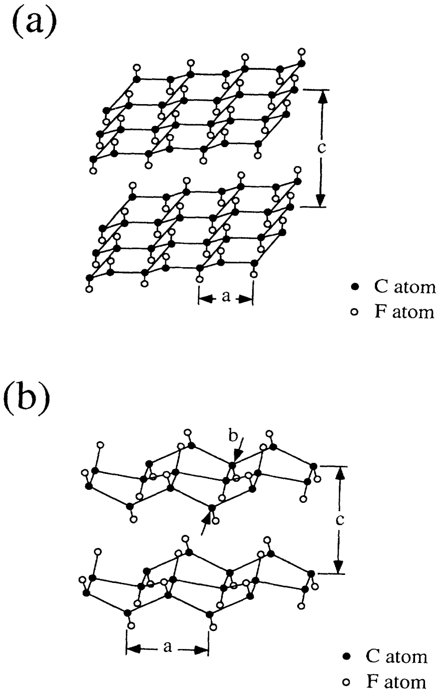

FIG. 1. Structure of graphite monofluoride $(CF)_n$ in its two conformations. Carbon atoms are black dots while fluorine atoms are in white. (a) In the chair conformation, a and c refer to the hexagonal unit-cell axes. (b) In the boat conformation, a, b, and c refer to the orthorhombic unit-cell axes.

On the other hand, the infinite array of *cis-trans*-linked cyclohexane boats [Fig. 1(b)] is the only alternative geometrical possibility that has been considered. The symmetry of the boat structure results in an orthorhombic crystal lattice which contains eight atoms (4F+4C) and belongs to the $Pmm2$ space group.

The *ab initio* results for the crystalline parameters of both conformations and the corresponding formation energies are shown in Table I. In the chair conformation, there is only one kind of C-C bond (between two carbon atoms which bind with fluorine atoms on different sides of the graphitic plane), while in the boat conformation there are two kinds of C-C bonds (between two carbon atoms which bind with fluorine atoms on different sides of the graphitic plane, or that bind with fluorine atoms on the same side of the graphitic plane). The theoretical values are 1.552 Å for the chair conformation, and 1.543 and 1.625 Å for the boat conformation. Note that the latter value is larger than the two others, likely due to the steric factor. The C-F bond length is nearly identical in both structures (1.37 Å).

Our results also confirm that graphite monofluoride is geometrically different from other intercalated compounds and also carbon-fluorine compounds, where graphitic planes are not distorted. Such puckering could, in part, account for the large calculated intersheet spacing

(c) of 5.7 Å, but this spacing is also due to a large van der Waals gap.[23]

The formation energy of the chair conformation (-10.66 eV per CF unit) is relative to the following chemical reaction:

$$F_2+\text{graphite}\leftrightarrow 2F(\text{graphite}) .$$

A comparison of this value with experimental data (cf. Table I) exhibits the well-known problem of overestimation the cohesive energy (and formation energy) by the

TABLE I. Values of crystalline parameters, carbon-carbon, and carbon-fluorine bond lengths (in Å), angles (deg), atomic positions (reduced coordinates), and formation energy relative to the F_2 molecule and solid graphite (in eV/CF unit) for the two conformations of graphite monofluoride $(CF)_n$. The first column contains the *ab initio* results obtained by the preceding theoretical method. The following columns are collections of best experimental evaluations relative to hypothetical $(CF)_n$ conformations.

$(CF)_n$	Theory	Experiment		
	Chair			
Hexagonal unit cell				
$a=b$	2.553[a]	2.53[b]	2.54[c]	2.57[d]
c	5.666[a]	5.76[b]	5.80[c]	5.85[d]
Atomic positions				
C	$(\frac{1}{3},\frac{1}{3},-z)$			
C	$(\frac{2}{3},\frac{2}{3},z)$			
F	$(\frac{1}{3},\frac{1}{3},-u)$			
F	$(\frac{2}{3},\frac{2}{3},u)$			
	with $z=0.042\,73$ and $u=0.284\,52$			
Bond lengths and angles				
C-C	1.552[a]	1.47[b]	1.54[c]	1.53[d]
C-F	1.37[a]	1.41[b]	1.39[c]	1.41[d]
C-C-C	110.7[a]	118.8[b]		109.3[d]
C-C-F	108.2[a]			
Formation energy				
	-10.6603[a]	-7.65[e]		
	Boat			
Orthorhombic unit cell				
a	4.511[a]	5.13[f]	4.11[g]	
b	2.527[a]	2.51[f]	2.47[g]	
c	5.673[a]	6.16[f]	5.76[g]	
Atomic positions				
C	$(x,\frac{1}{2},z)$			
C	$(\frac{1}{2}-x,0,-z)$			
C	$(\frac{1}{2}+x,0,-z)$			
C	$(-x,\frac{1}{2},z)$			
F	$(\frac{1}{4}-w,\frac{1}{2},u)$			
F	$(\frac{1}{4}+w,0,-u)$			
F	$(\frac{3}{4}-w,0,-u)$			
F	$(\frac{3}{4}+w,\frac{1}{2},u)$			
	with $x=0.180\,12, z=0.054\,92, w=0.002\,84$ and $u=0.289\,43$			
Bond lengths and angles				
C-C	1.543[a]	1.625[a]	1.54[f]	
C-F	1.364[a]	1.40[f]	1.64[g]	
C-C-C	114.1[a]	109.9[a]		
C-C-F	107.7[a]	102.8[a]		
Formation energy				
	-10.5155[a]	-7.65[e]		

[a] Present work.

[b] V. K. Mahajan, R. B. Badachhape, and J. L. Margrave (Ref. 11).

[c] D. E. Parry, J. M. Thomas, B. Bach, and E. L. Evans (Ref. 26).

[d] H. Touhara, K. Kadono, Y. Fujii, and N. Watanabe (Ref. 28).

[e] J. L. Wood, R. B. Badachhape, R. J. Lagow, and J. L. Margrave (Ref. 5).

[f] L. B. Ebert, J. I. Brauman, and R. A. Huggins (Ref. 10).

[g] P. Jr. Kamarchik and J. L. Margrave (Ref. 9).

DFT. As this overestimation of the cohesive energy is very large, it may also indicate that the experimental samples do not closely conform to the structures that have been investigated in this study.

The energetical difference between these two structures is 0.0725 eV/atom (in absolute value) in favor of the chair conformation, which will be considered, in the following, as the optimal structure. Even if this structure is energetically the most favorable, kinetic factors may govern the actual synthesis. In order to test this possibility, the potential barrier needed to transform the boat into the chair structure has been estimated by exchanging the position of two fluorine atoms as represented in Fig. 2(a) (concerted exchange). One possible transition path has been generated using a linear combination of the extreme atomic positions of the two states. The transition was performed in the boat conformation unit cell [cfr. Fig. 2(a)] by moving the fluorine atom (1), located over one carbon atom, above its nearest neighbor (1′). The corresponding fluorine atom (2) below the graphitic plane was shifted in the opposite way to reach the "empty" carbon (2′). The *ab initio* energy barrier of this path is 2.72 eV [cf. Fig. 2(b)] and must be considered as a maximal height for the potential barrier.

The actual transition path is likely different from our simple linear combination of positions. The error was estimated by relaxing the atomic coordinates at the top of the linear transition path, using the forces acting on the atoms in that geometry. This procedure only decreased the height by 0.106 eV, with residual forces (max: 0.01 hartree/bohr) five times smaller than the ones observed at the top of the linear transition path. We conclude from that transition path study that the boat conformation is a metastable one, separated from the chair conformation by a large energy barrier. The crossing of the graphitic plane by a fluorine atom was considered to be energetically impossible in the transition phenomena.

Although the structure of the material actually synthesized is unclear, the next section will focus on the electronic properties of the chair conformation only, assuming that this lowest-energy structure is at least the most abundant.

IV. ELECTRONIC PROPERTIES

The crystal structure of $(CF)_n$ was taken from the structural optimization established in the preceding section for the chair conformation. The C-C and the C-F bond lengths were assumed to be, respectively, 1.552 and 1.37 Å. The three-dimensional Brillouin zone is presented in Fig. 3.

The valence electronic charge density is shown in Fig. 4. The isodensity lines display the main features of bonding. The bonds between carbon and fluorine atoms are clearly presented in the density perpendicular to the graphitic planes in Fig. 4(a). The covalent bonds between carbon atoms are exhibited in the in-plane density in Fig. 4(b) and are quite similar to the natural graphite electronic charge density.[3]

In Fig. 5, the valence density of $(CF)_n$ minus that of a reference puckered graphite compound is presented. In this figure, the excess charge density induced by F has σ character at the expense of some loss of graphite π density. This result is consistent with the band structure results of Fig. 6, where it will be seen that the weakly antibonding component of the graphite π bands have been moved to band σ above the Fermi level. This result is in accordance with preliminary results obtained for $(C_4F)_n$ in the Rüdorff structure[25] with unperturbed graphitic planes.

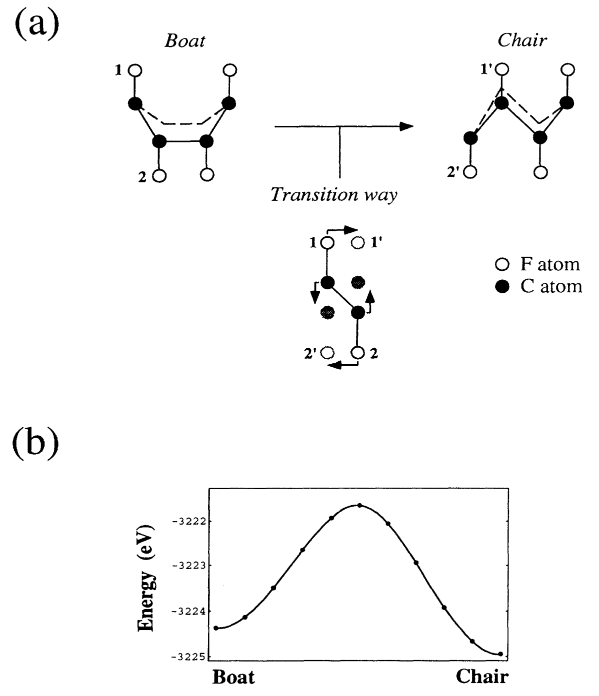

FIG. 2. (a) Crystalline representation of the transition from the boat to the chair conformation as discussed in the text. (b) Total energy as a function of the atomic coordinates in the corresponding transition. The curve is a polynomial interpolation between 11 calculated points.

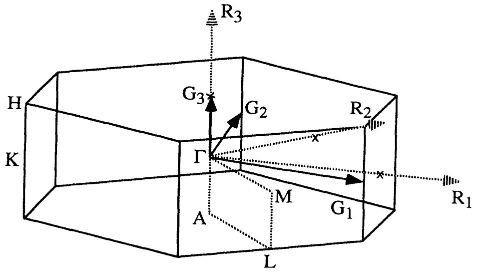

FIG. 3. Bravais lattice vectors (R_i), reciprocal lattice vectors (G_i), and Brillouin zone of the infinite array of *trans*-linked cyclohexane chairs. High-symmetry points are also presented and labeled with the usual Bouckaert-Smoluchowski-Wigner (Ref. 24) notation (Γ, A, H, K, L, M).

The self-consistent calculation of the density of charge allows the construction of the band structure. Figure 6

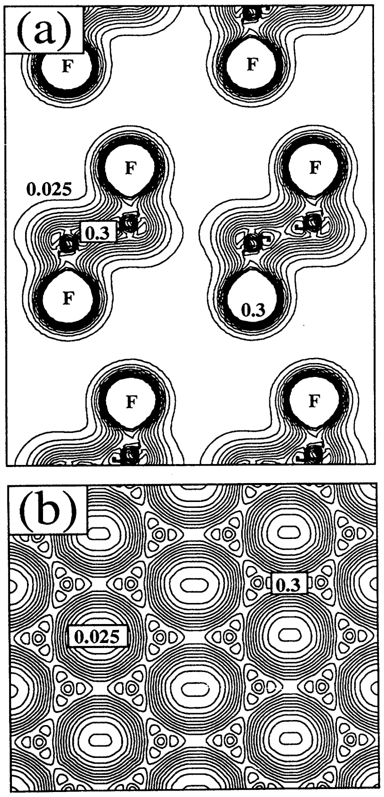

FIG. 4. Contour plot of $(CF)_n$—in the chair conformation—total valence density (a) in the (110) plane and (b) in the (001) plane passing through all the middles of C-C bonds. Contour levels are given in electrons/bohr^3 with a difference of 0.025 electrons/bohr^3 between curves. Peak density near the F atoms is omitted as it reaches the maximum value of 1.8 electrons/bohr^3. Atomic locations are denoted by F for fluorine atoms. [Note that the breaking of the trigonal symmetry in (b) is an artifact due to the discreteness of our two-dimensional mesh.]

shows the band structure of the first fifteen bands in different special directions of the Brillouin zone.

The F σ band is separated from the bottom of the C σ bands by a gap of 8.4 eV at Γ. The F π bands span a 6.8-eV range below the Fermi level, interacting with the lower π and upper σ bands of graphite; the lowest F π states have primarily π character. As all carbon atoms are involved in sp^3 bonds in this structure, a band gap is introduced near the Fermi level. The calculated direct band gap of 3.5 eV at Γ (2.7 eV at A) is consistent with the insulating behavior of $(CF)_n$.[26]

V. DISCUSSION AND CONCLUSION

In the present paper, the graphite monofluoride $(CF)_n$ has been characterized using first-principles techniques. We have determined the geometry of the boat and chair conformations, calculated the bond angles and bond lengths, and observed a larger bond length in the boat structure, for some C-C bonds. This effect has been ascribed to the steric factor. Because the energies of formation of the chair and boat conformations were close, we have also investigated a transition path (concerted exchange) between them.

As a result of that investigation, we have found three important energetic quantities: the formation energy (about 10.5 eV per CF in theory, 7.65 eV from experi-

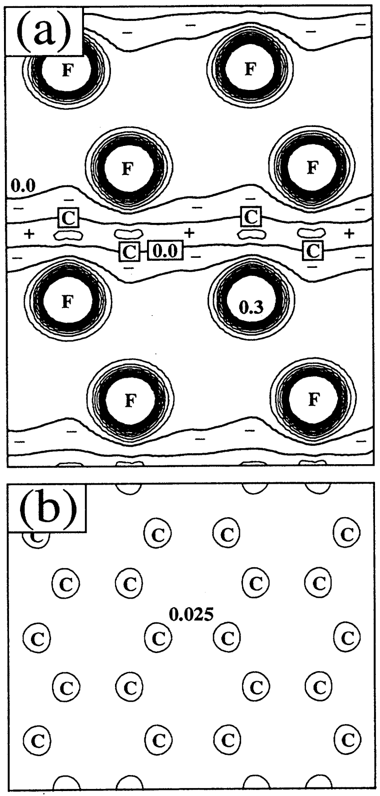

FIG. 5. Contour plot of total difference density of $(CF)_n$ (Fig. 4) minus that of reference graphite compound, shown in the same planes and same units as Fig. 4. Positive and negative zones of electronic density are labeled by + and −, respectively, between the lines of 0.0 electrons/bohr^3. Atomic locations are denoted by F and C for fluorine and carbon atoms, respectively. [Note that the breaking of the trigonal symmetry in (b) is an artifact due to the discreteness of our two-dimensional mesh.]

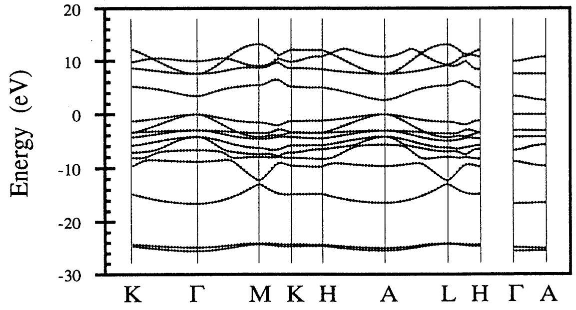

FIG. 6. Self-consistent band structure along different lines in the Brillouin zone for $(CF)_n$ in the chair conformation. The zero energy is positioned at the top of the valence band.

ment), the energy difference between the boat and chair conformations (0.145 eV per CF), and the energy barrier between the boat and chair conformations (2.72 eV for the linear concerted exchange of two F atoms). Although the chair conformation is the most stable one, the energy barrier is rather large, and we think that the material that is synthesized could depend on the condition of the synthesis. Indeed, the boat conformation material is metastable, but the formation energy is large enough to overcome the energy barrier, and a simulation of the intercalation process using molecular dynamics would be very interesting. In the final product, some disorder in the repartition of the alternation of C-F below and above the plane could be present, as well as islands of boat conformation in a mostly chair conformation material. On the other hand, the steric factor could prevent the kinetic formation of the boat conformation as well. These further issues are still difficult to address by today's *ab initio* methods, and will be left for future studies. In any case, we advise experimentalists to pay attention to the way their material has been synthesized, and not to assume a well-defined, unique, structure of $(CF)_n$.

In a second part of this study, we have examined the electronic properties of $(CF)_n$ in the chair conformation. The charge density has been calculated, as well as the band structure. As the carbon atoms have completely lost their aromatic nature, $(CF)_n$ has been found to be a good electrical insulator material, unlike other intercalated graphites.

In a larger framework, we note that the intercalation of graphite with fluorine is rather different from the intercalation with other species, not only because the planar graphitic geometry is distorted, but also because large energy barriers govern the in-plane diffusion of the intercalating species, making the final product likely dependent on kinetic effect, not only for the determination of the stage, but also for the determination of the in-plane geometry.

Also, the fluorination of graphite bears strong resemblance to the fluorination of C_{60}, giving $C_{60}F_{60}$: the hypothetical $C_{60}F_{60}$ with fluorine atoms both inside and outside the cage has been shown to be more stable than the species with all the F atoms outside the cage, with a similar puckering of the two-dimensional curved sheet.[27]

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