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Transition from direct band gap to indirect band gap in fluorinated carbon

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We studied phase stability, structural properties, and electronic band structures of graphite fluorides C_nF ($n=1,2,\ldots,6$) using density-functional theory with local density approximation. The calculation shows that C_nF with sp^3 bonding has a direct gap, when $n=1$ or 2. Even though C_nF with $n>2$ has not been identified experimentally, our calculation predicts that they become an indirect gap semiconductor.

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Fluorinated carbon materials[1,2] have attracted considerable attention in materials science. Graphite fluorides, such as carbonmonofluoride (CF) and dicarbonmonofluoride (C_2F), are typical stable materials.[3,4] They are synthesized by reacting fluorine molecules with various graphitic carbon systems. Graphite fluorides are used as solid lubricants[5,6] or as cathodes in lithium primary batteries.[7,8] CF is known experimentally as a transparent insulator. Rüdorff proposed a structural model,[4] which was later supported by x-ray experiments[1] as well as a first-principles calculation.[9] The model shows that a corrugated honeycomb plane of carbon terminated by fluorine atoms forms a unit plane, and such planes are stacked to build up the whole lattice. Every carbon atom is bonded with C or F via sp^3 covalent bonds. Thus, CF is a graphite intercalation compound with strong bonds between intercalants and graphite sheets. Interestingly, the existence of C_2F, which is regarded as the second stage of the fluorine intercalation compounds, has been confirmed.[1]

We report a systematic first-principles calculation for C_nF ($n=1,2,\ldots,6$). Fluorinated graphite is regarded as stacked diamond thin films covered by fluorine atoms. Thus, the properties of C_nF are expected to be similar to the properties of diamond. However, the most important result of our calculation is that C_nF has a direct band gap when n is 1 or 2. With increasing n, the band-gap structure of C_nF changes from the direct gap to the diamondlike indirect gap. In addition, our calculation shows that C_nF ($n>2$) can form stable structures, which have never been detected experimentally.

All calculations performed herein were based on density-functional theory[10,11] with local density approximation (LDA). A LDA functional form obtained by fitting Ceperly-Alder results for a uniform electron gas was utilized.[12,13] Norm-conserving pseudopotentials generated by the Troullier-Martins scheme were adopted to describe the electron-ion interaction.[14,15] The valence wave functions of the Kohn-Sham orbitals were expanded in a plane-wave basis set with a cutoff energy of 150 Ryd. To ensure accuracy of the pseudopotentials with this cutoff energy for both carbon atoms and fluorine atoms, we calculated a F_2 molecule, a CF_4 molecule, diamond, and graphite. The results gave bond lengths of molecules and solids with relative errors of less than 1.7%. Band structures of the solids reproduced previous results.[16] Actual calculations were done with the FHI package[17] for performing structure optimizations and band calculations. K points in our calculation were sampled by the Monkhorst and Pack scheme.[18] Structural optimization was performed until each component of the interatomic force became less than 0.001 Hartree/a.u.

A unit layer of C_nF is shown in Fig. 1(a). We calculated the A/A' stacking sequence [Fig. 1(b)] and A/A stacking sequence [Fig. 1(c)]. We designate C_nF with A/A' stacking sequence as hex-C_nF and C_nF with A/A stacking sequence as tri-C_nF. Hex-C_nF and tri-C_nF belong to the point group D_{3h} and D_{3d}, respectively. Hex-CF, hex-C_2F, and tri-C_nF, ($n=1,\ldots,6$) were investigated in the present study, however, hex-CF and hex-C_2F are known to exist, experimentally. For integration in Fourier space, the following numbers of k points reduced by symmetry were used for each structure: 12 k points for hex-CF and hex-C_2F, 42 k points for tri-CF and tri-C_2F, and 21 k points for tri-C_nF ($n=3,\ldots,6$). We confirmed that the number of k points was enough for convergence of total energy, structural properties, and electronic band structures.

We show the structural properties of hex-CF, tri-CF, hex-C_2F, and tri-C_2F. Optimized lattice constants are summarized in Table I. The in-plane lattice constant a of hex-CF and hex-C_2F determined by our calculation was almost identical to that determined experimentally. Moreover, the interplane lattice constant c determined by our calculation was about 2% smaller than that determined experimentally. The optimized bond length of C-F was 1.35 Å, and each C-C bond length was 1.54 Å ~ 1.55 Å for hex-CF and hex-C_2F. The lattice constant a and the bond length of tri-CF and tri-C_2F were almost the same as those of hex-CF and hex-C_2F.

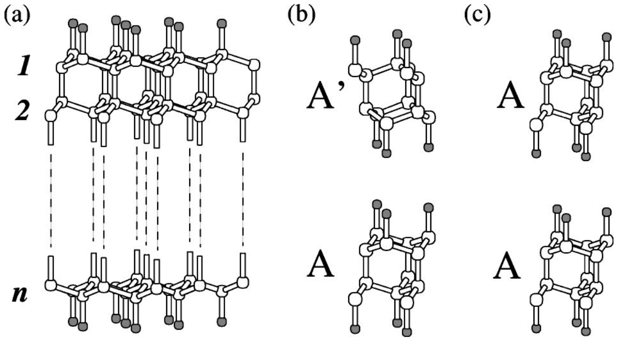

FIG. 1. (a) The unit layer of C_nF. Open circles and closed circles represent carbon atoms and fluorine atoms, respectively. The structure models of C_nF with the A/A' stacking sequence (hex-C_2F) (b) and C_2F with the A/A stacking sequence (tri-C_2F) (c) are also indicated.

TABLE I. Optimized lattice constants of hex-CF, tri-CF, hex-C_2F, and tri-C_2F. Experimentally observed values are shown in parentheses.

hex-CF	hex-C_2F
$a=2.55$ Å (2.53∼2.57 Å)	$a=2.52$ Å (2.51 Å)
$c=11.6$ Å (11.8 Å)	$c=15.8$ Å (16.2 Å)
tri-CF	tri-C_2F
$a=2.55$ Å	$a=2.52$ Å
$c=5.6$ Å	$c=7.7$ Å

However, the lattice constant c of tri-CF and tri-C_2F was 0.2 Å smaller than half that of hex-CF and hex-C_2F because of the atomic position of fluorine atoms. In hex-CF and hex-C_2F, a fluorine atom faces another fluorine atom in the nearest-neighbor layer, whereas in tri-CF and tri-C_2F, the fluorine atom does not face another in the nearest-neighbor layer. Our results for tri-CF reproduced the previous calculation.[9]

Band structures around a band gap of the optimized hex-CF and tri-CF are shown in Fig. 2. The valence-band top is set at zero energy. Hex-CF and tri-CF had a direct band gap. The conduction-band bottom (CBB) and the valence-band top (VBT) were located at the Γ point in the first Brillouin zone (1st BZ) for hex-CF. CBB and VBT were located at the A point for tri-CF. Change in the direct gap points is an effect of zone folding. Bandwidth of all the valence bands and the lowest conduction band on the Γ-A line were less than 1.5 eV. In particular, the bandwidth of the highest valence band was about 20 meV. Band structures of optimized hex-C_2F and tri-C_2F were similar to those of optimized hex-CF and tri-CF; hex-C_2F and tri-C_2F had a direct gap at the Γ point and the A point, respectively. The band gap of C_2F was larger than that of CF by about 1.1 eV.

We compared the total energy of optimized hex-CF and hex-C_2F with that of optimized tri-CF and tri-C_2F. The calculated total energy of tri-CF was greater than that of hex-CF by about 20 meV. For C_2F, the total energy difference was also about 20 meV. Thus, our calculation showed tri-CF and tri-C_2F to be more stable than hex-CF and hex-C_2F. However, experimental data suggest that CF and C_2F compounds have A/A' stacking sequence.[1,2] We speculate that difficulty in reproducing the stacking sequence is due to the van der Waals nature of the interlayer interaction. It is known that local density approximation (LDA) does not accurately describe the van der Waals interaction.[19] Interlayer interaction may be van der Waals–like because (1) a unit layer of C_nF has a band gap, (2) band dispersion of C_nF along the c axis is small, and (3) each layer is neutral without polarization.

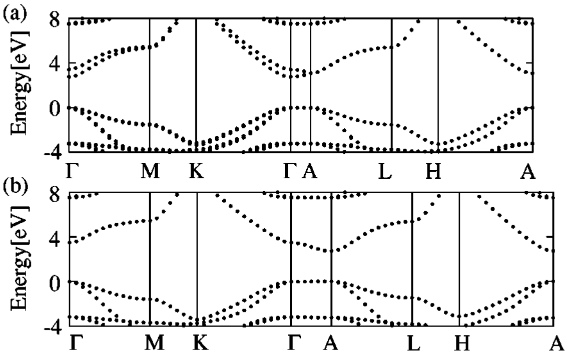

FIG. 2. The electronic band structure around the Fermi level of hex-CF (a) and tri-CF (b).

TABLE II. Optimized lattice constants a and c, the conduction-band bottom (CBB), and the valence-band top (VBT) in the 1st BZ for tri-C_nF ($n=3$, 4, 5, or 6).

	a	c	CBB	VBT
tri-C_3F	2.51 Å	9.9 Å	Γ	A
tri-C_4F	2.51 Å	11.7 Å	A	X''
tri-C_5F	2.50 Å	13.7 Å	A	X'
tri-C_6F	2.50 Å	16.0 Å	Γ	X'

Our results for CF and C_2F are in good agreement with experimental data except for the relative stability between the two kinds of stacking sequences. We now proceed to consider the structural properties and electronic band structures of extended compounds tri-C_nF with $n=3$, 4, 5, or 6. Calculations were made only for tri-C_nF because the structural and the electronic properties of C_nF compounds are essentially determined in a unit layer as we have shown.

Optimized lattice constants for tri-C_nF ($n=3$, 4, 5, or 6) are summarized in Table II. The optimized C-F bond length was 1.35 Å and each C-C bond length was 1.52 Å ∼1.54 Å. With increasing n, the lattice constant a of tri-C_nF ($n=1,\ldots,6$) approaches the distance between the second nearest-neighbor atoms of the cubic diamond, which by calculation is 2.50 Å.

Band structures around a band gap for optimized tri-C_nF ($n=2,\ldots,6$) are shown in Fig. 3. In the band structures, VBT is set at zero energy. With increasing n, there is a rise in the energy level of the lowest conduction band along the Γ-A line where the band begins to drop around the X' point (and the X'' point). Locations of CBB and VBT in the 1st BZ for tri-C_nF ($n=3$, 4, 5, or 6) are summarized in Table II. The width of the highest valence band on the Γ-A line was less than 20 meV. Our calculation showed that tri-C_nF ($n=3$, 4, 5, or 6) have indirect gaps. However, our preliminary calculation showed that C_3F with A/A' stacking sequence has a direct gap at the Γ point, because CBB and VBT in C_3F with A/A' stacking sequence are, like hex-CF and hex-C_2F, on the Γ point.

Let us systematically consider the band gap and the stability of tri-C_nF for $n=1$, 2, 3, 4, 5, 6, and ∞. Here, $n=\infty$ corresponds to the cubic diamond.

Figure 4(a) shows the band gap from VBT at the A point for tri-C_nF (denoted by E_A). In this figure, the smaller band gap for each n between the gap at X' point and X'' point from VBT are also shown (denoted by $E_{X'}$). The band gap of the cubic diamond E_g is shown in Fig. 4(a) and was calculated with the same accuracy as that of C_nF. The curves described by E_A and $E_{X'}$ cross at around $n=4$. $E_{X'}$ is smaller than E_A by about 20 meV at $n=4$.

Thus, our calculation predicts that C_nF compounds are a direct gap semiconductor for $n=1$ or 2 and a direct gap or an

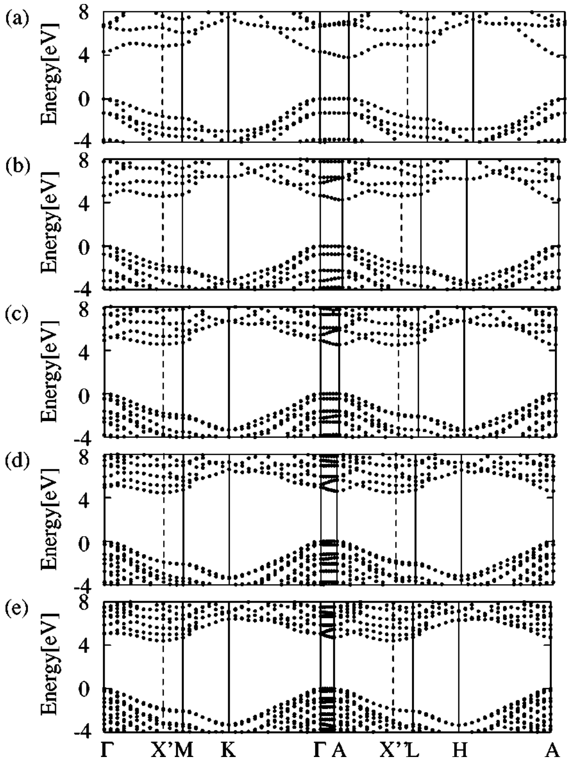

FIG. 3. The electronic band structures of tri-C_2F (a), tri-C_3F (b), tri-C_4F (c) tri-C_5F (d), and tri-C_6F (e) around the band gap.

indirect gap semiconductor for $n=3$, depending on stacking sequence, and an indirect gap semiconductor for $n \geqslant 4$.

Considering a unit layer of C_nF and its electronic states, the general trend of E_A and $E_{X'}$ can be explained as follows. States in the lowest conduction band on the Γ-A line are essentially the bonding state of two surface states in a unit layer. When the thickness of the layer increases, the bonding character is weakened and energy gain is reduced. Thus, E_A increases with increasing n. When n increases, the characteristics of bulk diamond should appear. Thus, conduction states at around X' or X'' points become stable, and $E_{X'}$ decreases with increasing n.

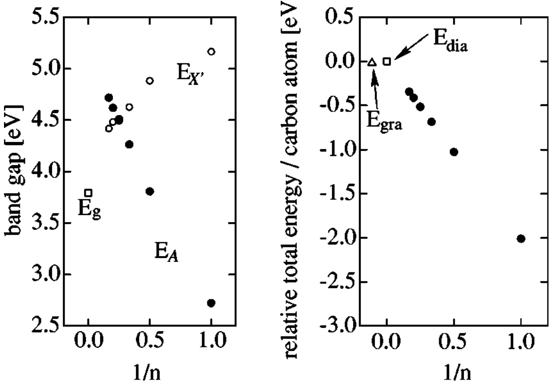

FIG. 4. (a) Band gap of C_nF $(n=1,\ldots,6)$, plotted as a function of $1/n$. Closed circles represent the band gap at A. Open circles represent the band gap at X' for tri-C_nF $(n=2,\ 3,\ 5,\ 6)$ and at X'' for tri-C_nF $(n=1,\ 4)$. The open square represents the band gap E_g of the cubic diamond. (b) The total energy par a carbon atom E_c for tri-C_nF plotted as a function of $1/n$. The definition of E_c is given in the text. E_{dia} and E_{gra} are the total energy par a carbon atom for cubic diamond and graphite with A/B stacking sequence, respectively.

Figure 4(b) shows the relative total energy per a carbon atom E_{c} for tri-C_nF. The total energy per a carbon atom for the cubic diamond E_{dia} and the graphite with A/B stacking sequence E_{gra} are shown in the figure also. In the figure, E_{dia} is set at zero. E_{c} is given by $E_{\mathrm{c}}=(E_{\mathrm{C}_n\mathrm{F}}-E_{\mathrm{F}_2})/2n$. $E_{\mathrm{C}_n\mathrm{F}}$ and E_{F_2} are the total energy per a unit cell containing $2n$ carbon atoms and two fluorine atoms for tri-C_nF, $(n=1,\ldots,6)$, and per an F_2 molecule. In our calculation, E_{gra} was lower than E_{dia} by a few meV, which matched a previous calculation.[20]

Values of E_{c} are roughly in proportion to $1/n$ and reach E_{dia} when $n=\infty$. From this relation, we conclude that C_nF compounds tend to become stable for smaller n. The total energy per a carbon atom of a CF_4 molecule was lower than E_{c} of tri-CF by about 8 eV. Thus, the most stable phase among our calculated phases was a C_4F molecule.

Experimentally, CF and C_2F compounds are formed by reacting graphitic carbon systems and F_2 molecules at temperatures ranging between 600 and 640 °C for CF and between 350 and 400 °C for C_2F.[2] With increasing temperature, fluorocarbon molecules such as C_4F and C_2F_6 are created from graphite and F_2 molecules. Thus, the yield of CF compounds decreases with increasing reaction temperature.[21]

Our calculations indicate that stable C_nF structures within the parameters of the LDA calculation can form; however, experiments show that carbon atoms prefer to make covalent bonds with fluorine atoms. Moreover, the curve of E_c versus n may explain why C-F bond formation is favored experimentally.

Herein, we describe the systematic first-principles calculation of graphite fluorides C_nF $(n=1,\ldots,6)$. Our calculations suggest that C_nF $(n>2)$, which have not been reported experimentally, can be synthesized. A type of band gap in C_nF compounds changes the direct gap to the indirect gap with increasing the stoichiometry (n), as shown in Fig. 4(a). The direct-indirect band-gap transition in C_nF differs from that in other systems such as $Al_xGa_{1-x}As$, where the phenomenon occurs by adding a third element, Al, to GaAs.[22,23]

LDA calculation generally underestimates the band gap. Thus, rescaling of the experimental band-gap value obtained from the LDA calculation is required to estimate the band gap in real materials. For diamond, our calculation yielded a band gap of about 70% the experimental value of 5.48 eV.[24] Accordingly, in real C_nF systems, the band gap is estimated to be about 1.4 times larger than the value obtained by our calculation. The estimated band gap of C_nF is within the ultraviolet region if the band gap is converted into wavelength. The estimation reproduces what is know experimentally, that CF and C_2F are transparent insulators.

If the component ratio in C_nF can somehow be controlled, C_nF compounds have a great potential for application. C_nF compounds may have potential utility in optical devices. With C_nF, it may be possible to design light-emitting diodes and lasers with wavelengths of approximately 0.2 $\sim$0.3 μm. Use of C_nF compounds as semiconductor devices will require further study on how the compounds are doped with electrons or holes. Doping may be achieved by a variety of methods including co-doping,[25] intercalation, and field effect.[26] Further studies on fluorination of related materials, like c-BN or BC_xN, will be fruitful. If the sequence of the C_nF layers can be controlled, a superlattice of direct-gap/indirect-gap semiconductor, like $\cdots/C_5F/CF/C_5F/\cdots$ may be created.

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