

# A Prospective Overview of the Potential of Fluorofullerenes as Host Materials for Intercalation Chemistry

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A theoretical survey of the ability of fluorofullerene crystals to act as host lattices for intercalation chemistry is proposed on a thermochemical basis and from the assumption that complete charge transfer between the fluorocarbon network and an electropositive intercalant species should occur upon insertion. A nearly exhaustive examination is performed throughout the fluoro[60]fullerene family, describing the influence of the intercalated element considered, stoichiometry, structural type, and fluorine content on the potential stability of an intercalated phase. Decomposition of the latter into a metal fluoride is then discussed. When extended to a general scheme, emphasizing the role played by the number of carbon atoms in the initial cluster, the present model shows that stable fluorofulleride salts may be expected to form in some cases. A final insight into the solid state properties of this class of materials, combined with a widespread range of potential applications, is provided.

## 1. Introduction

Among the numerous covalent derivatives of  $C_{60}$ , several individual fluoro[60]fullerenes have been isolated and their molecular structures solved,<sup>1</sup> mainly following the outstanding work of Taylor and co-workers in this field of fullerene chemistry. Fluorinated derivatives of higher fullerenes have also been identified,<sup>1a,2</sup> though their characterization has been far less detailed.

While the solubility of these compounds in conventional aprotic media and their high reactivity toward nucleophiles and dienes has seemed to restrict, so far, their short term interest to solution chemistry as synthons, it may be anticipated that their structural, binding, and electronic intrinsic features make them interesting precursors for solid state chemistry as well. Indeed, the dimensional character of fullerenes, understood in terms of long range tight binding in the space directions, is reduced with respect to their homocoordinated 2D analogue graphite, and interestingly, this seems to influence their chemical reactivity in a way that their fluorine addition pattern remains incomplete, as opposed to the presence of exclusively saturated carbons in standard covalent graphite fluoride  $(CF)_n$ . The question that may then naturally come to mind concerns the consequences of the persistence of a residual  $\pi-\pi^*$  scheme, and those of the inductive effect exerted on it by an electronegative element, on the chemical properties of the fluorination products obtained.

Transposed into the common language of condensed matter chemists, modifying the  $\pi$  electron density of the initial carbonaceous molecules via the partial addition of a halogen is equivalent to selectively introducing changes in the width and density of occupied states of the corresponding  $\pi$ -derived electronic bands, when the fluorocarbon network is concerned as a whole. The idea that intuitively asserts itself is whether chemical doping, a customary strategy employed for the modulation of the electronic properties of condensed phases,

may represent a potential mean to tune the Fermi level in such partly fluorinated materials. Hence, the application of the aforementioned molecular solids to intercalation chemistry appears as an attractive concept, remaining unexplored at this time. On the basis of a thermochemical approach of the problem, the present work sheds light on the stability of some still hypothetical  $M_nC_mF_x$  intercalation compounds and provides a step toward the speculative functionalities of fullerene fluoride-based advanced materials.

## 2. Calculation Methodology

**Background.** A detailed description of the modeling employed is given here. Since, in comparison to the unfluorinated carbon clusters, the presence of a strongly electronegative element should result in the emergence of lower energy unoccupied molecular levels, highly reinforcing the oxidizing character of the compounds, the most simple model probably lies in a donor–acceptor scheme, in which a doping process would result in the assignment of a net negative charge to the fluorinated molecules. The adequacy of such a charge transfer formalism finds a proper justification in the experimental observation of the high electron-withdrawing character of some isolated fluoro[ $m$ ]fullerene species, evidenced by the measurement of their individual extra-charge attachment characteristics in the gas phase<sup>3a–c</sup> or by their high electrochemical reduction potential and redox properties in solution.<sup>4</sup> For a better pertinence, the picture of a purely ionic fluorofulleride will however be restricted here to associated counterions belonging to the most electropositive families of elements.

Considering, in this first part, the sole case of the fluoro[60]fullerene series, the stability of such a salt-like  $(M^{q+}_n C_{60}F_x^{q-})$  condensed phase can then be established according to the change in Gibbs energy accompanying the intercalation reaction concerned, written with reference to one M atom:  $1/n C_{60}F_x(s) + M(s) \rightarrow 1/n M_n C_{60}F_x(s)$ . Since only solid phases are involved, the associated entropy change can be safely neglected and, if not too close to zero, the standard enthalpy of reaction  $\Delta_r H^\circ_n$

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should constitute a sufficient and appreciable guideline. It often happens to be possible to relate the former physicochemical property to various measurable or valuable thermodynamic quantities by means of a simple Hess law cycle, that is, the so-called Born–Fajans–Haber cycle, accounting for the formation of simple ionic crystals from the elements in their standard state. Therefore,  $\Delta_f H^\circ_n$  can be expressed as the sum of the sublimation and ionization energies of the initial reagents with the energy release associated with the condensation of the corresponding gaseous ions. Ionization potentials and enthalpies of atomization for elements *M* can be obtained from the usual references,<sup>5</sup> and according to the experimental data reported<sup>6</sup> for *x* = 0, 36, and 48, the standard molar enthalpy of sublimation of fluoro[60]fullerenes regularly decreases by 1.45 kJ/mol of added fluorine. The only steps requiring calculations then correspond to the charge transfer on the  $C_{60}F_x$  molecule (total electron affinity  $EA_x$ ) and to the cohesive energy of the final ionic solid.

**Modeling.** To address the previous point in its most general framework and to avoid a cumbersome and unnecessary separate analysis of a plethora of situations, the first approximation will consist in neglecting the individual structural features of a given  $C_{60}F_x$  molecule, therefore assimilated to a perfect spherical cluster with uniform atom density at the surface. The topological simplification introduced will be limited over the symbolic range *x* = 24–58, however, since the anisotropic distribution of surface addends in less fluorinated compounds, like  $C_{60}F_{18}$  or  $C_{60}F_{20}$ , was shown to induce distorted shapes.<sup>1a</sup> From a physical standpoint, the former smeared out approximation does not appear as crude as it may seem at first sight, since, for the few individual isomers isolated within the composition range considered above, the outer molecular profiles experimentally established<sup>1a,c,e–g</sup> indeed closely match spherical representations. Moreover, in the condensed state of fluorofullerenes, the frequent occurrence of a high crystal symmetry has to be associated with the presence of randomly oriented molecules in the unit cell,<sup>2a,d,7a–e</sup> making them, on average, true spherical units centered at lattice sites. Finally, when not consisting of a distribution in composition, pure fluorofullerene samples nearly always consist of a mixture of several isomers and/or stereoisomers, not necessarily isolable. The size and symmetry averaging principle of each molecular entity consequently appears as a physically motivated necessity.

Though the atomic arrangement in a solid turns out to be extremely difficult to anticipate, some simple steric and solid state chemistry considerations may help in the determination of a privileged structure for the final fluorofulleride which we are dealing with. Given the respective sizes of the host and guest species involved, it is clear that the structural architecture should lie on the “giant” fluorofulleride anion acting as the main building block. The basic structural features should consequently be governed by the setting of a stable anionic sublattice, abiding by the high coordination number and high density principles. Thus, the self-assembly of spherical units commonly results in the ABCABC or ABAB stacking sequences. This well-known phenomenon remains quite well observed among crystal data reported<sup>7</sup> from pristine (neutral) fluoro[60]fullerenes, with a marked preference for the cubic structure. A similar close-packed array will then be supposedly maintained within the final ionic structures envisaged, as a consequence of the non-negligible van der Waals binding energy which results from such an ordered configuration of high electron density anions. Hence, the tetrahedral (T) and octahedral (O) interstitial sites of such a matrix exhibit sufficient available space to accom-

modate alkali or alkaline-earth cations and most elements of the periodic table, causing a simple expansion or contraction of the unit cell, without distortion of the close-packed lattice of anions. The low cation/anion radii ratio is also in favor of the former provisional high symmetry structure, since the atomic scale ordering postulated allows for as short as possible anion–cation distances, thus minimizing the preponderant electrostatic energy. Finally, an empirical filiation may be established by referring to a family of parent phases, like the well-characterized<sup>8</sup> intercalation compounds of several high mass fullerenes with many elements. The arguments shortly developed above indeed seem to correctly describe the fundamental aspects of the crystal chemistry of the latter. In the following, one will therefore focus on the stability of  $M_nC_{60}F_x$  solid phases with pseudo  $Fm\bar{3}m$  or  $F\bar{4}3m$  symmetries, assuming progressive and single occupation of the T and O available cavities of a face-centered Bravais lattice of spherical  $C_{60}F_x^{p-}$  anions. Further refinement in the structural description adopted, related to off-centered positions in the interstitial voids, has not been taken into consideration, but it is expected that such relaxation effects should not induce too much energy difference in regards to the ideal atomic arrangements hitherto considered. These latest should therefore constitute a very useful starting point to assess a first overall picture of the potential of fluorofullerenes as host materials.

**Parametrization: The Solid.** The determination of the internal energy of the final intercalated solid, relative to the state of the free ions, can be treated from the classical theory of ionically bonded crystals,<sup>9</sup> the ability of which in providing remarkably good estimates of the cohesive energies and associated lattice properties has long been known. The main advantage of such an approach is its analytical simplicity and, as a corollary, its minimal computational cost, compared to quantum-chemical treatments, which has enabled a first set of more than 800 different cases to be examined in detail, according to the fluorination level of the  $C_{60}$  molecule and intercalated element considered. Thus, the cohesive energy *U* of a crystal is seen as resulting from the sum of additive and independent pairwise potentials, describing the different types of interactions between ions:

$$U = U_{\text{electrostatic}} + U_{\text{ion-ion repulsion}} + U_{\text{van der Waals}} + U_{\text{vibrational}}$$

With the substructure presently lying on a packing of very large spheres, the resulting interionic separations rapidly increase and the amplitude of the successive interactions (other than Coulombic) sharply drops on a short range. Therefore, only interactions between first neighbors need to be considered here. The vibrational part of the energy, usually small, can be safely neglected and will be compensated by the use of some room temperature crystal data during the parametrization of the model. The weak van der Waals binding contribution can be considered as arising mostly from the correlation of the electronic motions between the large, electron rich  $C_{60}F_x^{p-}$  molecular anions. Accordingly, by grouping the former attractive term of dipolar origin with the anion–anion repulsive term and by introducing the above-mentioned simplifications, the expression retained for the lattice energy of the ionic solid in standard conditions, relative to the number *n* of intercalated species, simply reduces here to

$$U^n(a) = \frac{1}{2} \sum_{i,j \neq i} q_i q_j e^2 / r_{ij} + \sum_{O,T} Z(n) \cdot \phi(r_{O,T}) + \frac{1}{2} Z' \cdot \phi'(r_k)$$

with each separation distance *r* being expressed in units of the

cell parameter  $a$ . The first quantity represents the electrostatic energy of the crystal, the second term stands for the whole of overlap repulsive forces which oppose the interpenetration of the nearest neighbor anion and cation electron shells and  $Z(n)/Z'$  denote coordination numbers.  $\phi'$  is a function accounting for the sum of the attractive and repulsive potential energies of interaction (non-Coulombic effects) between two  $C_{60}F_x^{p-}$  molecular anions at distance  $r_k$  apart. The equilibrium conditions are thereafter determined by minimizing the total energy of the system.

The part of the cohesive energy arising from the global interactions between the anionic clusters can be treated as in the case of the homologous non-intercalated molecular solid. In this context, the classical Lennard-Jones potential happens to fail in a correct prediction of the elastic properties of hollow-core sphere lattices, since the resulting calculated isothermal volume compressibilities of any  $C_m$  fullerite, for instance, indeed exceed by 3–6 times the experimental values reported. By taking into account the topological characteristics inherent to such kinds of molecular objects, Girifalco<sup>10a</sup> derived a more appropriate expression of their pair interaction energy, but heavy to handle and with too many unknown constant terms when extrapolated to a set of concentric heteroatomic layers.<sup>10b</sup> The interactions under consideration have therefore been parametrized via the analytically convenient Morse potential, involving suitably adjusted factors to be determined from crystal data. With reference to the cell parameter  $a$ ,

$$\phi'(r_k) = \epsilon_x [1 - \exp(-k(a/\sqrt{2} - 2R_x))]^2 - 1]$$

This form offers a much stiffer variation of the associated potential well, more adapted to the present situation. The bond dissociation energy  $\epsilon_x$ , according to the fluorination level  $x$ , is assigned a value corresponding to one-sixth of the sublimation enthalpy of the  $C_{60}F_x$  compound, corrected for the pressure–volume expansion product. As already mentioned, an almost linear dependence of the evolution of  $\Delta_{\text{sub}}H^\circ$  with  $x$  can be deduced from the literature data.<sup>6</sup> The potential energy of interaction varies as a function of the departure from the equilibrium distance  $2R_x$  in the pristine (undoped) fluorinated material, where  $R_x$  represents the average hard-sphere radius of the molecule with the fluorine content  $x$ . The distances of closest approach in several fluoro[60]fullerene crystals are currently available<sup>7</sup> from which a uniform variation of  $R_x$  at a rate of  $2.1 \times 10^{-3}$  nm/F atom can be determined. The constant  $k$  can be expressed as a function of the cell parameter, cohesive energy, and bulk modulus of the non-intercalated fluorinated phase, from the second derivative of  $\phi'$ . Recent results by Touhara and collaborators<sup>11</sup> on the  $C_{60}F_{36}$  and  $C_{60}F_{48}$  solid phases have palliated the lack of experimental data under pressure on such compounds and enabled the bracketing of  $k$  within  $15 \pm 5$  nm<sup>-1</sup>. This median value has been adopted as a universal constant for any fluorinated medium of that kind. For comparison, the characteristic value of the same factor is found to fall in the narrow range  $11 \pm 2$  nm<sup>-1</sup> for structurally parent stacking of hollow spheres, represented by isotypic (fcc)  $C_m$  fullerites, in which case the relevant literature data required for the calculation of  $k$  are abundant.<sup>12a–e,13,14</sup>

At this stage, the standard methodology employed becomes sufficiently academic that no further details may be necessary here to specify the Madelung and short range anion–cation overlap repulsive energies. The remaining function and numerical terms entering the lattice energy are available as Supporting Information, according to the various structures considered,

which differ by the nature and number of interstitial sites occupied. The refinement of the undetermined parameters has been done by applying the global two-body scheme developed up to here to some parent isostructural  $M_nC_{60}$  ionic salts, a family of compounds chemically as close as possible to the hypothetical  $M_nC_{60}F_x$  phases studied here, and for which basic solid state properties are readily accessible.<sup>15</sup> The hard-sphere radii used are quoted in standard tables<sup>16</sup> for the cations and have been constrained to the above-mentioned outer molecular radius  $R_x$  for the anion.

**Parametrization: The Guest–Host Electron Transfer.** The last step consists in evaluating the energy required to add additional negative charges on the  $C_{60}F_x$  molecule. Mass spectrometric techniques have made possible the study of electron attachment in the gas phase and a precise experimental bracketing of electron affinities via charge exchange reactions. Electrochemical data in solution can also provide formal information in this field, since the reduction potential reflects the energy amount required to add extra electrons on a given solvated species. An examination of the few published works<sup>3,4b–d</sup> concerning the energy associated with such a charge transfer from some individual  $C_{60}F_x$  species shows that, to a good approximation, the first electron affinity  $EA_x(p = 1)$  is monotonically incremented by 0.03 eV per fluorine atom added to the  $C_{60}$  molecule. No experimental data or theoretical calculations are available concerning the higher one-electron affinities of any fluorofullerenes, but it has been known<sup>17a</sup> since the early 1960s that the positive or negative ionization energies of extended aromatic systems can be satisfactorily evaluated from a macroscopic-like description of their molecular capacitance in a continuum model. Inheriting Smith's original idea<sup>17a</sup> of adding an intramolecular Coulomb contribution to account for the destabilization of electronic states, the formalism has still recently been successfully generalized to any multiply charged system, in which charged sites are quite distant and rather well localized. Hence, it has been shown<sup>17b</sup> that the modification in the potential experienced by valence electrons can be very efficiently determined from a classical treatment of the discrete electrostatic interactions exerted by negatively charged sites, provided the mutual interelectronic separations can be identified. Such a simple way to quantify the internal Coulomb energy has since proved a major advance in the study of isolated multiply charged anions. Since in the general case of addended fullerenes, the opportunity of extra-charge delocalization at the surface of the spheroidally shaped nano-objects happens to be reduced, due to a decrease in the size of the conjugated system formed by the remaining C=C double bonds, such a physical model of localized interacting point charges should then be preferred. The scheme here adopted consists of the rigorous calculation of the Coulomb energy difference between two successive electronic configurations, corresponding to the most energetically favorable distribution of  $(p - 1)$  and  $p$  point charges over a spherical surface. The successive one-electron affinities  $EA_x(p > 1)$  can then be reasonably estimated by modifying the value of the first  $EA_x$  by a quantity corresponding to the aforementioned electrostatic energy difference. The sphere radius to be considered corresponds to the inner carbon–carbon bond frame, where extra charges are confined. As the F/C ratio increases, the more and more pronounced influence of the nearly sp<sup>3</sup> character of each halogenated atom results in an inflation of the carbon skeleton, which contributes to move the charges away from each other. Looking back again at the sole case of the fluoro[60]fullerene series, the dependence in regard to the fluorine content, of the average inner radius



$R_{\text{int}}^{\text{int}}$ , must be specified. A linear variation of the latter has then been assumed between the inner radii of a nonfluorinated  $\text{C}_{60}$  molecule and of an ideal (hypothetical)  $\text{C}_{60}\text{F}_{60}$  entity. Hence, for a truncated icosahedron,  $R_{\text{int}}^{\text{int}}$  is given by  $1/2 L(9\tau^2 + 1)^{1/2}$ , with  $\tau$  being the golden ratio and  $L$  being successively the average carbon–carbon bond length in the unfluorinated (0.142 nm) and in the completely fluorinated molecule (taken as the standard 0.154 nm long C–C single bond).

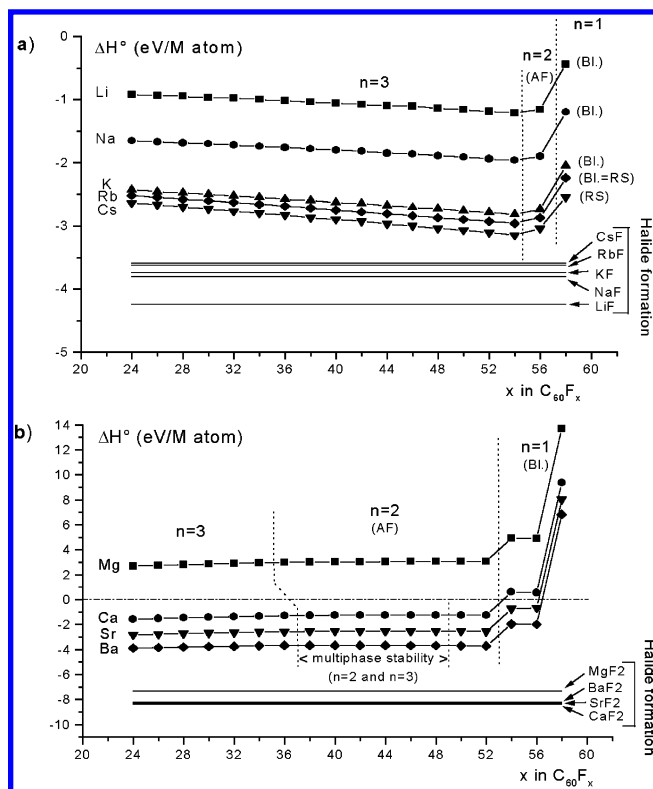
The forthcoming paragraph deals with some particular cases of the charge transfer aspect.  $\text{C}_{60}$  halogenation involves a break in conjugation and a subsequent reduction in the density of  $\pi$  states. Thus, according to a qualitatively acceptable rigid description of the electronic structure, the corresponding energy diagram can be divided into a set of novel low lying C–F and C–C  $\sigma$  bonds plus a distinct subset of residual  $\pi$  bonds and into a higher lying and symmetrically equivalent block of unoccupied antibonding states. Transposing the present picture to the case of the most highly fluorinated species ( $x > 52$ ) implies that part of the transferred electrons may need to occupy common molecular orbitals, as the number of remaining individual  $\pi^*$  LUMO levels becomes insufficient. The repulsive electrostatic interaction of diametrically opposed point charges, confined to a unique carbon–carbon double bond site, then gives a rough estimation of the related additional energy ( $\sim 11$  eV). Furthermore, if more than two electrons are to enter the same surface bond site ( $p > 4$  for  $x = 56$  or  $p > 2$  for  $x = 58$ ), the exclusion principle requires one to resort to higher acceptor levels of  $\sigma^*$  nature and account must be taken, beside an electrostatic term of the previous type, of the  $\pi^*-\sigma^*$  energy gap, which is estimated to at least 2.5 eV from spectroscopic investigations reported<sup>18</sup> on highly fluorinated [60]fullerene. The magnitudes involved here appear so drastically high in regard to the final energy summation over the global thermodynamic cycle that destabilization is foreseen, making then such borderline cases beyond consideration.

### 3. Preliminary Results and Discussion

In the following, the present modeling has been applied to the theoretical study of the intercalation into some  $\text{C}_{60}\text{F}_x$  host lattices of the elements of the first and second column (except Be) of the periodic table, that is, the most appropriate to the formation of ionic salts. The results of the calculations performed are summarized (Figure 1) in terms of the associated reaction enthalpies  $\Delta_r H^\circ_n$ , when  $n = 1, 2$ , or 3 of the available interstitial sites are occupied. Globally and not surprisingly, the downshift observed upon going from Li to Cs and from Mg to Ba parallels the evolution in the ionization and sublimation energies of these elements.

**Potential Stability of the Intercalation Compounds.** A preliminary comment has to be made concerning the relative stability, at constant doping level, of the different possible ionic arrangements. For the  $\text{M}_1\text{C}_{60}\text{F}_x$  and  $\text{M}_2\text{C}_{60}\text{F}_x$  phases, the zinc blende and antifluorite structural types, which are associated with the highest Madelung constants, represent by far the most stable configurations, and the other cation ordering possibilities need not be considered anymore for these stoichiometries. The only exception arises for the large size monovalent cations  $\text{Rb}^+$  and  $\text{Cs}^+$ , in which case a rock-salt  $\text{M}_1\text{C}_{60}\text{F}_x$  structure prevails over the zinc blende type, though the energy difference nearly vanishes near  $x = 56-58$ .

The first point to be examined is now obviously the occurrence of negative values of the calculated heats of reaction, the reference criterion for thermodynamic stability at this level of the study. It turns out that only the formation of Mg-based



**Figure 1.** General illustration of the intercalation/fluoride formation competition across the fluoro[60]fullerene series (the lines between points are guides to the eye). The number  $n$  of intercalant ions, quoted in each zone, either corresponds to the only stable intercalated phase (1a,b) or to the lowest-lying one when several phases can exist (1b). AF = antifluorite, BL = zinc blende, RS = rock-salt structural type.

intercalation compounds seems to be precluded, since it is strongly endothermic.

In the second place, the relative stability of the intercalated phases has been determined regarding the number  $n$  of intercalant ions in the fluorocarbon matrix, by examining the opportunity, thermodynamically speaking, of some disproportionation or decomposition reactions. Normalized to one acceptor molecule and for a doping level of  $n' > n$ , these ones can be successively formulated:  $\text{M}_n\text{C}_{60}\text{F}_x(\text{s}) \rightarrow n/n'\text{M}_n\text{C}_{60}\text{F}_x(\text{s}) + (1 - n/n')\text{C}_{60}\text{F}_x$  and  $\text{M}_n\text{C}_{60}\text{F}_x(\text{s}) \rightarrow \text{M}_n\text{C}_{60}\text{F}_x(\text{s}) + (n' - n)\text{M}$ . The changes in enthalpy accompanying the former chemical transformations are therefore  $n(\Delta_r H^\circ_{n'} - \Delta_r H^\circ_n)$  and  $n\Delta_r H^\circ_n - n'\Delta_r H^\circ_{n'}$ , respectively. Whatever the cation considered in the alkali-metal series, the first quantity is almost systematically found negative if  $n' = 3$  and, from the thermochemistry point of view, the only phase remaining to take in consideration in this case is then  $\text{M}_3\text{C}_{60}\text{F}_x$ , with the cryolite type structure. A few exceptions appear at extreme fluorination levels only, when the energy penalty related to the acceptance of many electrons by the anions becomes too high. The same still holds true throughout the alkaline-earth cation series at middle and extreme fluorination regimes, but the simultaneous stability of several doping levels ( $n = 2$  and  $3$ ) can also be encountered in between, as depicted on Figure 1. Only the phase presenting the lowest  $\Delta_r H^\circ_n$  per M atom has been retained for illustration in this case, but the energy differences remain of weak amplitude each time.

**Intercalation versus Defluorination.** The last and probably most important question to be addressed is the competitive aspect, on an energy scale again normalized to one metal atom, of the following  $1/n\text{C}_{60}\text{F}_x(\text{s}) + \text{M}(\text{s}) \rightarrow 1/n\text{C}_{60}\text{F}_{x-qn}(\text{s}) + \text{MF}_q$  defluorination process, with respect to the so far assumed intercalation reaction. The related enthalpy change  $\Delta_r H^\circ_{\text{def}}$

depends on the difference in the standard enthalpies of formation of each left- and right-hand component of the chemical system.  $\Delta_f H^\circ_{C_{60}F_x}$  has been conveniently approximated for the present purpose as  $\Delta_f H^\circ_{C_{60}} + \alpha x$ . It is found that an additional energy amount of  $\alpha = -209$  kJ/mol of added fluorine fits in an acceptable way the scarce available thermochemical data issuing from direct calorimetry measurements<sup>19a-d</sup> and from a mass spectrometry study<sup>19e</sup> of fluorine exchange in the gas phase from fullerene molecules. Hence, using standard notations,  $\Delta_f H^\circ = \Delta_f H^\circ_{MFq} - q\alpha$ . It should be noted that, with the initial number of F atoms being always even, the product of the defluorination process should be formally written as a 50% to 50% mixture of  $C_{60}F_{x-(n+1)}/C_{60}F_{x-(n-1)}$  phases when  $n$  is odd and a monovalent cation is involved, leaving of course the result of the preceding enthalpy summation unchanged. A global comparison of the relative energies associated with the two competing patterns concerned is illustrated on Figure 1. It can be clearly seen that chemical reduction via the loss of fluorine is favored in any case, in regard to reduction via electron transfer.

**Comment.** The success of the predictive aspects developed here will obviously strongly depend on the accuracy of each level of approximation, especially regarding the electron gain energetics. Somehow, the previous conclusion that no stable fluoro[60]fulleride may be expected, at least from light alkali metals, seems corroborated by the experimental evidence of alkali-fluoride formation when  $C_{60}F_x$  compounds are used as cathode materials in lithium batteries<sup>20a,20b</sup> or are exposed to potassium vapor.<sup>20c</sup> A close energy balance between intercalation and defluorination is situated in the [high F/C ratio + heavy alkali ions] zone, where the increase in the heats of formation of alkali-metal fluorides and the increase of the total electron affinity with  $x$  both converge to make the scenarios almost competitive.

#### 4. Generalization

The present theoretical approach has been further extended to a tentative systematic study, and in this second part, a schematic view on the intercalation chemistry of any fluorinated fullerene  $C_mF_x$  solid phase has been considered. The forthcoming estimates lie on a restricted number of cases, though, limited to the most favorable situations previously encountered, including an optimized and fixed  $M/C_m$  molar ratio and a fluorine content permitting the distribution of not more than one extra charge per remaining double bond, respectively.

**Global Parametrization.** To achieve the present purpose, it turns out to be necessary to introduce ad-hoc assumptions and approximations to palliate the nonexistence of experimental data over the whole range of precursors involved and, accordingly, to first define the effective van der Waals radius  $R_{m,x}$  of each spheroidal fluorinated molecule, that will determine the equilibrium distances in the intercalated solid. For any  $[m]$  fullerene, assuming a uniform and invariable surface density of carbon atoms at the core level of the cage makes the corresponding internal radius  $R_m^{\text{int}}$  vary as  $bm^{1/2}$ , where  $b$  is a constant. The external radius  $R_m$  is obtained by adding to the previous term the typical "thickness"  $t$  of a carbon atom in a fullerene molecule. The  $b$  and  $t$  coefficients can then be determined by fitting the presumably exact phenomenological variation law of the outermost molecular radius of a  $C_m$  cluster to an empirical radii scale issued from crystallographic data gathered on hard-sphere packing of high mass fullerenes.<sup>12,13c</sup> At last, the superposition of a surface fluorine layer, whose average outward steric extension is proportional to the sole F/C ratio (independent

of the fullerene cage and already determined from the fluorinated  $C_{60}$ -based systems), gives the final size  $R_{m,x}$  of the  $C_mF_x$  molecule.

The successive charge transfers on the molecular anions have been treated in the same way as above. As a starting condition, the previous local point charge model needs to be modified with the help of a general expression quantifying the first electron affinity  $EA_m(p = 1)$  of any nonfluorinated  $C_m$  fullerene. A simple relation, experimentally well-verified and originating from basic electrostatic principles on conducting hollow spheres, was proposed earlier by Seifert and co-workers.<sup>21</sup> As the F/C ratio becomes nonzero, the evolution of the first electron affinity  $EA_{m,x}(p = 1)$  has been further supposed to parallel that in the fluoro[60]fullerene series. This approximation seems reasonable in view of the sparse mono-electronic transfer data found in the literature<sup>3b-d,4b</sup> and involving the  $C_{70}$  fluoride family. In tackling the problem of the successive one-electron affinities  $EA_{m,x}(p > 1)$ , the inflation rate of the inner carbon frame upon fluorination has been assumed to be maintained, with reference to the fluorinated derivatives of  $C_{60}$ . This implies the conservation of the  $R_{m,x}^{\text{int}}/R_m^{\text{int}}$  proportionality factor at constant F/C, keeping in mind that the determination of  $R_m^{\text{int}}$  has been seen just before.

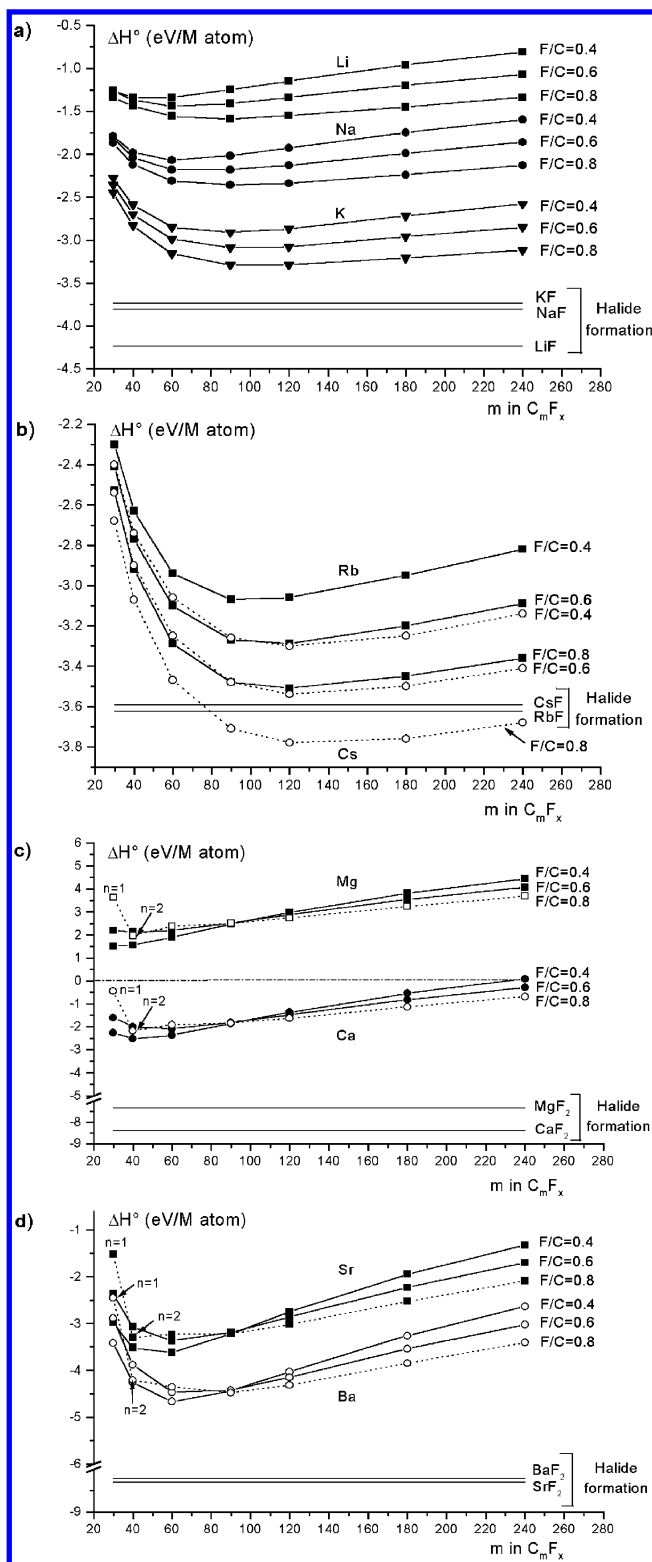
The last point to be addressed remains the quantitative evolution of the enthalpy of sublimation of the pristine  $C_mF_x$  host material. From the numerous results reported,<sup>13</sup> it can be firmly established that  $\Delta_{\text{sub}} H^\circ_{C_m} = 0.03$  eV/C atom at 298 K. The influence of the fluorine content on this value has then again been supposed to mirror the F/C dependence in the  $C_{60}F_x$  series. The hypothesis introduced at this level is actually of small importance, since the most part of the energy involved in the dissociation of the initial host lattice is recovered in the formation of the condensed ionic phase, so that this term should nearly cancel in the final sum over the cycle.

**Results.** Whether the existence of a stability zone for a salt-like  $(M^{q+}_n C_m F_x)^{qn-}$  compound is precluded or not has been established with respect to the intercalation versus defluorination competition already described in the first part. The C–F bond dissociation energy should not depend to a great extent on the carbon frame, and consequently, neither should the difference in the enthalpies of formation of the initial and final  $C_m F_x / C_m F_{x-qn}$  fluorofullerenes, when the carbon–halogen bond cleavage is considered. Whatever the fullerene series, the change in enthalpy corresponding to the loss of fluorine can therefore be assumed as nearly constant.

The general behavior foreseen has been illustrated in Figure 2. Some stability zones can be clearly distinguished for heavy alkali metals. Extrapolating the results summarized in Figure 2 shows that increasing the fluorine level above 80% on high mass fullerenes may even still notably downshift the energetics of intercalation (between  $-0.1$  and  $-0.2$  eV/M atom), with respect to that of alkali-halide formation.

**Comment.** When applied to the formation of simple binary compounds where purely ionic bonding predominates, the accuracy of the ionic model often falls below a few percent error in the determination of the lattice properties currently examined. Though the present work is not intended to provide such precise values, efforts have been made for factors entering the parametrization to entirely originate from experimental results, thus limiting effects inherent to arbitrary values or hazardous procedures, which should help in minimizing aberration within the structural context adopted.

The pertinence of simple electrostatic models to describe the tuning of levels in the HOMO–LUMO regions has now become



**Figure 2.** General illustration of the intercalation/fluoride formation competition across the fluoro[*m*]fullerene series. Small deviations from the values of Figure 1 arise for *m* = 60, due to the use of a general formula in calculating the first EA of the nonfluorinated cluster (see text). When not specified, the number of intercalant ions is *n* = 3. (2b) data for Rb (■) and (○) Cs metals.

widely taken for granted. For fullerenes, such a scheme has been shown to fairly reflect the ionization potential or electron affinity evolution,<sup>21</sup> with respect to experimental measurements. One might then expect the correction here introduced for partial localization in the case of derivatized fullerenes, so as to

correctly describe the intramolecular electron–electron repulsion, to lead to a similar level of accuracy.

The general trend searched for appears sufficiently reliable, therefore, and clearly shows that the defluorination and intercalation processes can be competitive on an energy scale. On such grounds, the potency of some fluorofullerenes as host materials for intercalation chemistry seems tantalizingly conclusive.

## 5. Concluding Remarks

It is hopeful that the present general perspectives will stimulate the emergence of novel research topics, owing to the unconventional valence and dimensional characteristics inherent to the hypothetical derivatives investigated here. Attention may be drawn on the fact that their practical interest could be strongly reinforced by facile processing of the precursor host solid, whose underlying molecular nature renders its solubility or sublimation easy. Fluorofullerides can consequently be attractive for use as coatings or thin films as well as bulk materials.

Hence, intercalation almost invariably implies to refer to solid state electrochemical devices, most of the time. The atypical anion–cation radii ratio yields a permeated network which may facilitate interstitial cation mobility in the intercalated phase, a property at the source of solid electrolytes and of their use in sensors. The presence throughout the sublattice of numerous large cavities, affording possibilities of transient multiple occupancy, may also contribute to provide paths for easy ion migration, thereby enhancing ionic conductivity. If the use of fluorofullerenes as cathode materials for second generation batteries seems precluded, owing to the high molar weight of each cell component which would render the mass capacity severely limited, initially pale and transparent films of fluorinated high mass fullerenes might be of interest for electrochromism, provided cathodical coloring can be detected in the course of doping. One of the most interesting features of the doped phases may precisely reside in their optical properties, since the trapping of electrons (via the charge transfer effect) at the isolated conjugated polycyclic “islands” remaining at the surface of the acceptor molecule should almost certainly generate chromophore moieties. Indeed, the filling of some  $\pi^*$  states offers new opportunities of symmetry-allowed electronic transitions, within the residual set of  $\pi^*$  antibonding MOs. This phenomenon involves a moderate energy difference between the discrete levels concerned and thus increases the probability of obtaining spectral characteristics covering narrow parts of the visible spectrum. This is clearly and analogously best exemplified by the usual intense absorption of aromatic cyclic hydrocarbon anion radicals in the visible region.<sup>22</sup>

Despite the change induced in the Fermi level and associated density of state upon chemical doping, no enhancement of the electron transport properties is expected a fortiori, since the large intermolecular separation in the solid would result in poor intersite overlap, strongly limiting the possibility of an itinerant behavior of the transferred charge carriers. Spin localization is not without interest, however, and the study of arrays of stabilized multivalent anions, carrying high magnetic moments likely to induce magnetic ordering, remains of practical and fundamental interest.

Finally, though the synthesis of fluorinated fullerenes with a single definite stoichiometry has proved extensively difficult to achieve most of the time, the latter problem may be circumvented, since the regular progression observed in each characteristic makes the conclusions drawn so far applicable to fluorofullerene mixtures with an average  $C_mF_x$  composition.



**Supporting Information Available:** Table of some numerical values involved in the lattice energy calculation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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