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Raman, infrared and n.m.r. studies of the graphite hydrofluorides $C_xF_{1-\delta}(HF)_\delta (2 \leqslant x \leqslant 5)$

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Raman spectra of $C_xF_{1-\delta}(HF)_\delta$ ($x/\delta \approx 12$) show bands at 1600, 1355 and 839 cm^{-1}, which are attributed to graphite-like vibrational modes of the carbon atom sheets. The infrared spectra show, in addition to graphite-like bands, absorptions at 1270 and 1100 cm^{-1}, which are attributed to C–F stretching. Variable contact-time cross-polarized magic-angle spinning ^{13}C nuclear magnetic resonance spectra (c.p.m.a.s.^{13}C n.m.r.) have been obtained for $x = 2.05$ and 3.70. In both spectra, two peaks ($+135/10^6$ and $+88/10^6$ chemical shift from TMS) are seen, which are attributed, respectively, to graphitic and C–F carbons. The ratio of graphitic to C–F carbon atoms has been found to be 1.6(2):1 in $C_{2.05}F_{0.82}(HF)_{0.18}$. The carbon atom sheets in $C_xF_{1-\delta}(HF)_\delta$ appear to be very similar to those in pristine graphite. The bonding of fluorine to carbon is highly ionic. Bonding models are discussed.

1. INTRODUCTION

It is well known that graphite and fluorine gas do not interact at room temperature and ordinary pressures. At higher temperatures (380–600 °C), the lamellar compounds $(C_2F)_n$ and $(CF)_n$ are formed, in which the carbon atoms are disposed in puckered sheets (Rüdorff & Rüdorff 1947*a*; Kita *et al.* 1979). In the presence of HF, graphite is spontaneously intercalated by fluorine, at room temperature. The first accounts (Rüdorff & Rüdorff 1947*b*) of such a reaction describe the first stage compounds $C_xF_{1-\delta}(HF)_\delta$, where $3.57 < x < 4.03$ and δ is assumed to be small. Later studies (Lagow *et al.* 1972, 1974) have shown that δ is indeed appreciable (0.27–0.34). In our preliminary studies of this system (Mallouk & Bartlett 1983), we reported the compositions C_xF ($2.0 \leqslant x \leqslant 5$ to 6). Analysis specifically for HF content has established that these compounds contain approximately one hydrogen atom for every twelve carbon atoms, and are better represented as $C_xF_{1-\delta}(HF)_\delta$ (where δ is *ca.* $1/12x$).

The structure of 'tetracarbon monofluoride' (C_4F) has been discussed by Rüdorff & Rüdorff (1947*b*) and Rüdorff (1959). While it cannot be unequivocally demonstrated from their X-ray powder diffraction data, they proposed that in C_4F the carbon atom sheets were flat and that the fluorine atoms made close (*ca.* 1.4 Å†) contacts to the carbons. Their finding of high electrical conductivity for $C_4F_{1-\delta}(HF)_\delta$ also supported their notion that the carbon atom sheets were planar. Recent work in these laboratories (Mallouk & Bartlett 1983; Mallouk 1983) has established that chemical fluorination of graphite, to compositions $C_xF_{1-\delta}(HF)_\delta$, $x \geqslant 2.3$, may

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† 1 Å = 10^{-10} m = 0.1 nm.

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be reversed entirely (to graphite) by electrochemical means. This reversibility is also consistent with the carbon atom array not being very much distorted away from planarity by fluorination.

The vibrational spectra presented here for $C_xF_{1-\delta}(HF)_\delta$, together with c.p.m.a.s. ^{13}C n.m.r. spectra, establish that the carbon sheets are indeed planar, even in the limit $x \approx 2$, where the compound is an electrical insulator. These spectra also indicate that the binding of fluorine to carbon is the same throughout the entire range of composition; fluorine atoms are found to be attached singly to carbon atoms via weak, semi-ionic bonds. The Raman spectra establish that the domains of fluorine atom ordering in the *ab* plane are about 50–100 Å in extent. ^1H n.m.r. spectra have shown that the proton-containing species within the graphite binds to the host lattice. Motion or exchange of that species is slow at 298 °K.

2. EXPERIMENTAL

(*a*) *Preparation*

$C_xF_{1-\delta}(HF)_\delta$ was prepared by reaction, at 20 °C, of graphite powder (Union Carbide SP-1) with F_2 (at 2 atm†) and gaseous HF (for $x \geqslant 2.4$), and from graphite, F_2 (at 2 atm), and liquid HF (for $x \approx 2.0$). The samples were pumped out for 24 h at the conclusion of the reaction and elemental analyses for carbon and hydrogen were made. The hydrogen was determined as HF by pyrolysing *ca.* 100 mg $C_xF_{1-\delta}(HF)_\delta$ at 1000 °C and condensing the volatiles into a trap containing KOH solution; potentiometric back-titration with HCl solution gave the hydrogen content. Typical compositions were: $C_{2.05}FH_{0.18}$ (C/H = 11.6), $C_{2.70}FH_{0.22}$ (C/H = 12.3), and $C_{3.75}FH_{0.33}$ (C/H = 11.4).

(*b*) *Vibrational spectra*

Transmission infrared spectra of $C_{2.5}F_{1-\delta}(HF)_\delta$ were recorded on a Nicolet 8000 high-voltage Fourier-transform infrared spectrometer. The sample was prepared by grinding a graphite chip in such a way that the *c*-axis lay in the plane of the resulting thin flake. The flake was then intercalated by interaction with fluorine and HF vapour at 20 °C. This arrangement exploits the high conductivity anisotropy of graphite and its compounds; electromagnetic radiation may be transmitted through the graphite flake provided its electric vector is aligned parallel to the *c*-axis. Normally, vibrational modes that have in-plane components are not observed. In $C_{2.5}F_{1-\delta}(HF)_\delta$, however, the *ab* plane conductivity is low enough for all the infrared active modes to be seen.

Raman spectra were recorded on a J–Y Ramanor spectrometer, using an argon ion laser (488.0 nm) excitation, for several compositions of $C_xF_{1-\delta}(HF)_\delta$. The spectral resolution was 2 cm^{-1}. Typically, 100 scans were taken and added together from powder samples that were contained in quartz X-ray capillaries; the quartz line at 808 cm^{-1} provided a fiducial marker in the spectra.

(*c*) *N.m.r. spectra*

^{13}C c.p.m.a.s. spectra of $C_{2.05}F_{1-\delta}(HF)_\delta$ and $C_{3.70}F_{1-\delta}(HF)_\delta$ were obtained by using a modified Nicolet NT-150 spectrometer equipped with a home-built solids probe and associated high-power pulse amplifiers and matching networks. The 150 MHz console proton decoupler was re-tuned and modified for operation at 141.2 MHz for ^{19}F spin locking and decoupling. An Amplifier Research Model 200L amplifier operating at 100 W was used as the final stage

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† 1 atm = 101325 Pa.

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of the decoupler to provide a Hartmann–Hahn match of 50 kHz. Contact times were varied from 100 μs to 20 ms with pulse repetition times of about 1 s. Samples were spun at the magic angle in 10 mm o.d. Delrin rotors at about 2.8 kHz. The ^{13}C chemical shifts were referenced to the aromatic resonance of a solid hexamethyl benzene external standard, which was taken as $132.2/10^6$. The ^{1}H n.m.r. spectrum of $C_{2.15}F_{0.83}(HF)_{0.17}$ powder was recorded at 20 °C on a home-built spectrometer operating at a proton resonance frequency of 360 MHz.

(*d*) *X-Ray powder diffraction*

Powder patterns were taken on a General Electric Precision Camera with a 45 cm circumference, and with use of Ni-filtered CuK_α or Zr-filtered MoK_α radiation.

3. RESULTS AND DISCUSSION

(*a*) *Vibrational spectra*

The Raman spectra of powdered samples of $C_xF_{1-\delta}(HF)_\delta$ are shown in figure 1 for several values of x. The spectra are all virtually identical to the spectrum of graphite itself (Solin 1980), which has a Raman mode at 1581 and an infrared mode 848 cm^{-1} corresponding, respectively, to in-plane and out-of-plane motions of the carbon atoms. In addition to these, a broad band at 1355 cm^{-1} is observed. Such a band is seen in the Raman spectrum of graphite powder that is poorly ordered or that has been disordered by grinding. It has been attributed to a zone

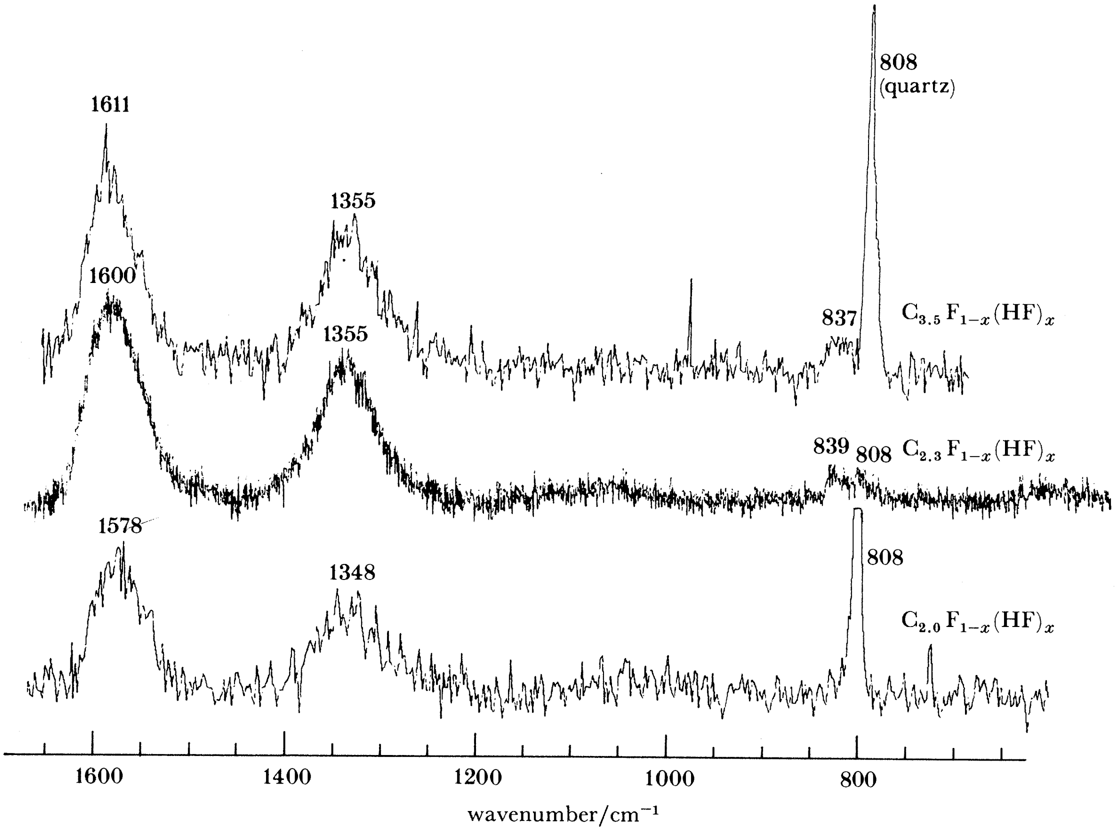

FIGURE 1. Raman spectra of first stage graphite hydrofluorides.

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boundary mode that is Raman-inactive in crystallites of large extent (Tuinstra & Koenig 1970); it corresponds to an in-plane ring-breathing motion. The intensity of this band relative to the graphite E_{2g}-like band at 1600 cm^{-1} indicates the extent of the ordered domains in the *ab* plane (Tuinstra & Koenig 1970). The domain size, for $C_xF_{1-\delta}(HF)_\delta$ is in the range 50–100 Å. A slight shifting (*ca.* 30 cm^{-1}) towards lower frequency of the *ca.* 1600 cm^{-1} band is found for the highest fluorine concentrations, indicating a very slight weakening of the carbon–carbon bonding; this observation is in accord with the small increase in bond distance (by 0.006 Å) inferred from the crystallographic *a*-spacings (Mallouk & Bartlett 1983), for compositions in which the C/F ratio is nearly two. The intensity of the C–F stretching band is expected to be low in the Raman spectrum. It is barely discernible near 1100 cm^{-1}.

The transmission infrared spectrum of $C_{2.5}F_{1-\delta}(HF)_\delta$ (figure 2) shows, in addition to the graphite-like bands situated at 1587 and 850 cm^{-1}, an exceptionally strong absorption at *ca.* 1100 cm^{-1} and a shoulder at 1270 cm^{-1}. Both are attributed to C–F stretching vibrations. Comparison of these with the C–F stretching frequencies in $(CF)_n$ and $(C_2F)_n$ (1219 and 1221 cm^{-1}, respectively (Rüdorff & Rüdorff 1947*b*)) suggests that for the bulk of fluorine in $C_xF_{1-\delta}(HF)_\delta$ (represented by the *ca.* 1100 cm^{-1} band) the C–F bond order is lower than in the other carbon fluorides. The 1270 cm^{-1} band may arise from a small concentration of $>CF_2$ groups at the edges of the carbon-atom layers.

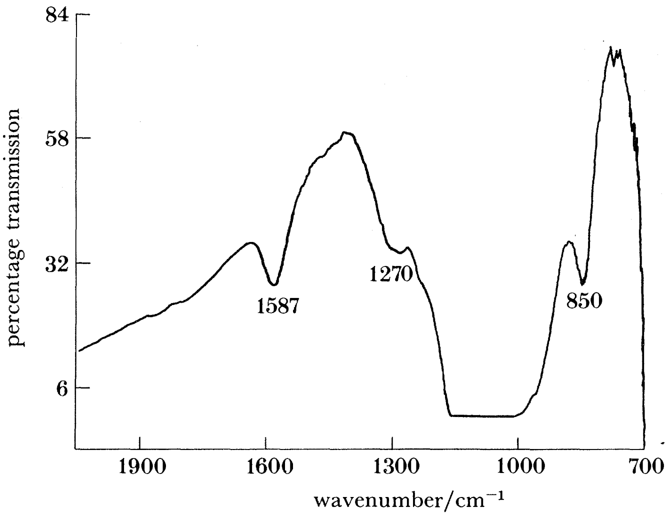

FIGURE 2. Infrared spectrum of $C_{2.5}F_{1-\delta}(HF)_\delta$.

The presence of graphite-like vibrations, occurring at practically the same frequency as in graphite itself, establishes the planarity of the carbon sheets in $C_xF_{1\delta}(HF)_\delta$, even at C/F ratios of two.

(*b*) ^{13}C *n.m.r. spectra*

Magic angle spinning spectra of $C_xF_{1-\delta}(HF)_\delta$ powders were obtained, by using $^{19}F \rightarrow {}^{13}C$ cross polarization, for $x = 2.05$ and $x = 3.70$. In both spectra (figure 3) two peaks, separated by $47/10^6$, are observed, the similarity of the spectra suggesting the same bonding environments for both compounds. The low-field peak ($\delta = 135/10^6$ chemical shift from TMS) exhibits spinning sidebands, displaced $\pm 97/10^6$ from the central peak, indicating a large chemical shift

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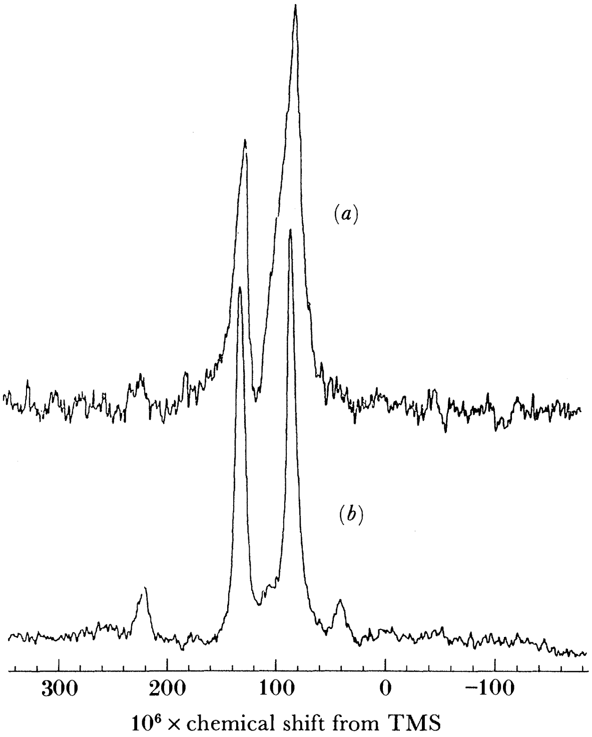

FIGURE 3. ^{13}C n.m.r. spectra of (a) $C_{3.7}F_{1-\delta}(HF)_\delta$ and (b) $C_{2.05}F_{1-\delta}(HF)_\delta$.

anisotropy for these carbon atoms. This chemical shift and shift anisotropy are characteristic of aromatic (i.e. graphite-like) carbon. The high-field peak is attributed to carbon atoms bound to fluorine. In addition, a small peak at $112/10^6$ has been resolved in some of the spectra. This peak is attributed to a small concentration of $>CF_2$-type carbon atoms. These are probably found at the edges of the grains.

The ratio of the aromatic and C–F carbons in the sample may be determined by varying the $^{19}F \rightarrow {}^{13}C$ cross-polarization contact time. The spectral intensity arising from the ith carbon spins is given by (Mehring 1976)

$$I_i = kN_i(1 - T^i_{CF}/T_{1\rho})^{-1}\,[\exp(-t/T_{1\rho}) - \exp(-t/T^i_{CF})].$$

Here t is the contact time, $T_{1\rho}$ is the fluorine spin-lattice relaxation time in the rotating frame, k is an instrumental constant, N_i is the relative concentration of the ith spins, and T^i_{CF} is the characteristic cross relaxation time, which depends on the strength of the dipolar coupling (and hence the distance) between the ith carbon atoms and their fluorine atom nearest neighbours. The variable contact time spectrum of $C_{2.05}F_{0.82}(HF)_{0.18}$ is shown in figure 4. Note that the high-field peak is magnetized more quickly than the graphitic peak, indicating, for the high field nuclei, bound fluorine.

Table 1 shows the observed and calculated spectral intensities for $C_{2.05}F_{0.82}(HF)_{0.18}$ as a function of contact time. The C–F peak fits quite well to a T_{CF} of 0.10 (2) ms and a fluorine $T_{1\rho}$ of 6.0 (5) ms. For the graphitic peak, a satisfactory fit can only be obtained from the superposition of approximately equal concentrations of carbon spins with short (0.40 (5) ms) and long (2.50 (8) ms) values of T_{CF}. The relative concentration of the graphitic and C–F

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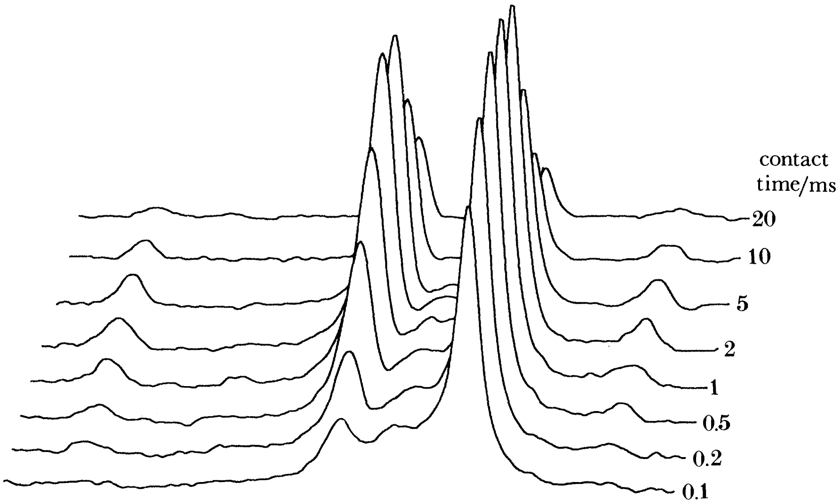

FIGURE 4. Variables contact time $^{19}F \rightarrow {}^{13}C$ cross-polarization n.m.r. spectra of $C_{2.05}F_{1-\delta}(HF)_\delta$.

TABLE 1. OBSERVED AND CALCULATED ^{13}C N.M.R. INTENSITIES FOR $C_{2.05}F_{0.82}(HF)_{0.18}$

contact time/ms	low-field peak		high-field peak	
	I(obs.)	I(calc.)	I(obs.)	I(calc.)
0.10	285	189	867	674
0.20	351	338	902	910
0.50	627	623	1000	1000
1.00	788	818	915	926
2.00	906	890	754	784
5.00	729	715	432	475
10.00	348	361	181	206
20.00	166	72	76	39

For low-field carbons: $T^1_{CF} = 0.40$ (5) ms, $N_1 = 0.78$ (10); $T^2_{CF} = 2.49$ (8) ms, $N_2 = 0.79$ (10).
For high field carbons: $T_{CF} = 0.10$ (2) ms, $N = 1.00$.
For fluorine: $T_{1\rho} = 6.0$ (5) ms.

carbon atoms is found to be 1.6 (2) : 1. This is in good agreement with the value expected (1.50), assuming that the HF present is not bound to carbon, and that only two-centre C–F bonds are formed (and not three-centre F–C–F bonds, as we had previously allowed as a plausible bonding model) (Mallouk & Bartlett 1983).

The ^{13}C n.m.r. spectra are consistent with structures that, like Rüdorff's (Rüdorff & Rüdorff 1947*b*; Rüdorff 1959), allow for planar carbon-atom sheets and attachment of carbon to only one fluorine atom at a time. The persistence of graphitic carbon, even at C/F ratios approaching two, suggests that delocalized π-bonding is maintained in the carbon-atom sheets.

(*c*) *The role of* HF *in* $C_xF_{1-\delta}(HF)_\delta$

The persistence of HF in first-stage graphite hydrofluorides is noteworthy. When $C_{2.05}F_{0.82}(HF)_{0.18}$ is heated to 140 °C and subjected to a dynamic vacuum for two days, only about half of the HF is removed; the crystallographic *c*-spacing of the material so treated undergoes a contraction from 6.25 (2) to 5.92 (2) Å. The bulk of the remaining HF is not removed at temperatures below 300 °C. When $C_xF_{1-\delta}(HF)_\delta$ is exposed to liquid HF and not pumped, a *c*-axis expansion of 0.5–0.6 Å is found, corresponding to the uptake of one molecule

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of HF for every 11–14 carbon atoms. Electrochemical cells employing $C_xF_{1-\delta}(HF)_\delta$ with HF/NaF as the electrolyte generally have internal resistances about $\frac{1}{10}$ to $\frac{1}{20}$ of those with aqueous alkali fluoride or organic (for example, propylene carbonate/$LiPF_6$) electrolytes. Clearly, the interaction of HF with the graphite fluoride is strong. It appears to bind tenaciously to the host lattice and can assist in the removal of fluoride ions. The most likely HF binding mechanism is through hydrogen bonds to the C–F fluorines, which appear, from X.p.s. studies (Mallouk & Bartlett 1983), to bear a partial negative charge. The ^1H n.m.r. spectrum of $C_{2.15}F_{0.83}(HF)_{0.17}$, shown in figure 5, provides a measure of the strength of this interaction. The linewidth ($37/10^6$) is indicative of hindered rotation or diffusion of the proton-containing species at 20 °C, which occurs with an activation enthalpy of about 46–50 kJ mol^{-1}. Alternatively, the protons in $C_xF_{1-\delta}(HF)_\delta$ could be present in ionic species such as HF_2^-, which are relatively fixed in the gallery and so cannot undergo rotation or exchange at 20 °C. This model appears unlikely, however, since significant concentrations of anions in the galleries, and equivalent hole concentrations in the carbon sheets, would be expected to give rise to electronic conduction in $C_{2.0}F_{1-\delta}(HF)_\delta$. The observed resistivity of the latter is in excess of 10^7 Ω cm.

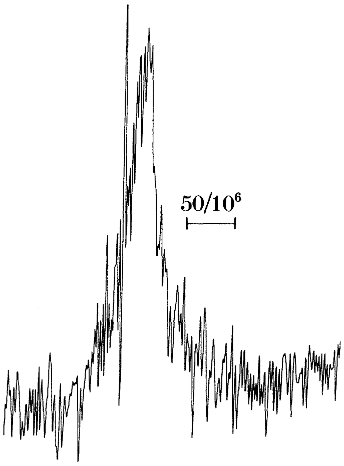

FIGURE 5. Proton n.m.r. spectrum of $C_{2.15}F_{0.83}(HF)_{0.17}$.

(*d*) *Structural models for* $C_xF_{1-\delta}(HF)_\delta$

X-ray powder data (Mallouk & Bartlett 1983), together with the vibrational and ^{13}C n.m.r. spectra, establish that the carbon atoms in $C_xF_{1-\delta}(HF)_\delta$ are arranged in virtually undistorted, planar sheets, as are the carbon atoms in graphite. Raman spectra of $C_xF_{1-\delta}(HF)_\delta$ suggest that the fluorine atom array is ordered in small (50–100 Å) domains. Twinning and haphazard stacking of such domains can account for the observed loss of diffraction intensity (table 2) for *hkl* ($l \neq 0$) reflections with increasing Bragg angle.

There are two notable features of the X-ray powder data for $C_xF_{1-\delta}(HF)_\delta$. One is the marked increase in c_0 spacing (Mallouk & Bartlett 1983) for x values less than 3. The other is the disappearance of *hkl* reflections for x values less than 3. Evidently there is close packing of the sheets for x values of three or greater. That, as x approaches a value of 2, only *hk*0 and 00*l* reflections are observed, implies that there is little or no registry of positioning of one sheet relative to its neighbours. Because of the electrochemical reversibility of the synthesis of

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TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR $C_{2.49}F_{1-\delta}(HF)_\delta$

(The radiation source was MoK_α; $a = 2.457$ (3), $c = 6.01$ (5) Å. No corrections were made for absorption or thermal motion.)

intensity(1)	$1/d^2$(obs.)	$1/d^2$(calc.)	*hkl*	*I*(calc.)(2)	*I*(calc.)(3)
v.v.s.	0.0277	0.0277	001	—	—
v.v.s.	0.2204	0.2209	100	1000	1000
v.s.	0.6618	0.6626	110	459	347
w.	0.8855	0.8835	200	64	24
m.w.	1.5553	1.5461	210	42	42
m.w.	1.9944	1.9878	300	52	39
w.	2.6525	2.6504	220	30	26
v.w.	2.8603	2.8713	310	13	6

(1) Abbreviations; w., weak; s., strong; v., very; m., medium.
(2) *hk*0 Intensities were calculated using $x, y = \pm(\frac{1}{3}, \frac{2}{3})$ for C and F.
(3) Intensities calculated using carbon $x, y = \pm(\frac{1}{3}, \frac{2}{3})$ and fluorine $x, y = \pm(0.365, 0.635)$.

$C_xF_{1-\delta}(HF)_\delta$ ($x \geqslant 2.6$), it is reasonable to assume that the F ligands can easily relocate to provide for their greatest separation, at any composition. Figure 6 shows the F ligand distributions to be expected for C_3F and C_2F stoichiometries (F signifying F and HF in these instances). The C_3F arrangement provides for interlocking of the layers and close packing; the C_2F arrangement does not. Since the van der Waals diameter of fluorine is about 2.7 Å, it is likely that the occurrence of two C–F linkages on the same side of the sheet in *meta* ring positions would be sterically unfavourable; the closest F–F contacts in such an arrangement would be only 2.46 Å. For this reason the *meta* contact models are not included in figure 6.

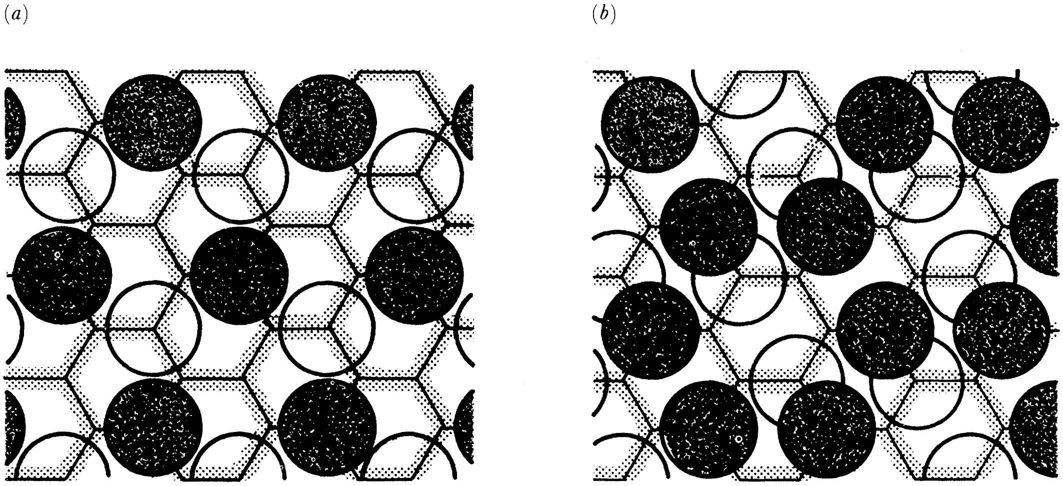

FIGURE 6. Structural models for (*a*) C_3F and (*b*) C_2F. (The unshaded circles represent the fluorine atoms on one side of a carbon-atom sheet and the shaded circles represent the fluorine atoms of an adjacent sheet in positions of closest packing.)

The C–F bond in $C_xF_{1-\delta}(HF)_\delta$ is clearly unusual. The fluorine atoms bound to the carbon cannot withdraw significant electron density from the graphite σ or π-system since the carbon-atom sheets have practically the same dimensions and stretching frequencies as in graphite itself. The bonding molecular orbital composed of fluorine sp and carbon p_z atomic orbitals is of appropriate symmetry to overlap with the neighbouring carbon p_z orbitals, and

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so some π-bonding will be maintained. The C–C π-bond order may be preserved if the carbons make, in the language of valence bond theory, one-electron dative bonds to the fluorine atoms. These electrons bestow a partial negative charge on the fluorine atoms and are at the same time used in π-bonding within the carbon network. Such π-electrons employed in the binding of F atoms must be strongly localized near the fluorine. Charge carriers (electrons) must therefore have low mobility at such centres in the π system. This can account for the conductive character of C_3F and the insulating character of C_2F, if the structural models shown in figure 6 are valid. For the C_3F model it is necessary to assume that the F atom attachment on one side of the sheet is *ortho* to that of the other. In that case chains of the non-fluorinated π system remain to provide the high-mobility pathways for the charge carriers.

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