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Electronic charge transfer in stage-2 fluorine-intercalated graphite compounds

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The optical reflectivity in the visible and the near infrared of fluorine-intercalated highly oriented pyrolytic graphite compounds was studied as a function of fluorine concentration between C_9F and $C_{3.4}F$. Between C_8F and C_4F we studied the samples which exhibited a stage-2 structure. The experimental results were analyzed in terms of the Blinowski-Rigaux two-dimensional (2D) model, which yields directly the plasma frequency and the scattering time of the free charge carriers. It is found that, for fluorine concentrations below that of C_6F, the plasma frequency increases with increasing concentration and has a maximum at C_6F. At higher fluorine concentrations, the plasma frequency decreases rather sharply. This anomalous behavior is explained in terms of a two-acceptor-state model. Below the fluorine concentration of C_6F, there is only one acceptor state with an energy $E_1 = E_F - 1.034$ eV. A second acceptor state forms when the concentration of fluorine increases further. Each additional fluorine transfers two other fluorines from the first acceptor state to the second, the energy of which is $E_F - 0.84$ eV. The behavior at still higher fluorine concentrations is different again and indicates the formation of covalent bonds. Our analysis indicates that in the limit of low fluorine concentrations the charge transfer is one electron per six fluorine atoms. It drops as the concentration increases and is $\frac{1}{8}$ per fluorine at C_6F and $\frac{1}{16}$ at C_4F. These results agree very well with the two-acceptor-state model.

INTRODUCTION

In the past few years, it has been found that, upon exposure of graphite to fluorine in the presence of minute amounts of impurities (e.g., HF, AsF_5, etc.) conductive compounds are obtained.[1-5] It is the family of $C_{nl}FM_x$, with $nl > 3$ and $0 < x < 0.1$, where n is the stage index. M represents impurities such as metal fluorides (MgF_2, CuF_2),[4] hydrogen fluoride,[3,5] or metal hexafluorides.[3] These materials serve as catalysts which promote the intercalation process. In addition to the high conductivity, these compounds are also characterized by a rather strong interaction between the fluorine and carbon layers. The Raman spectra[6] of graphite-fluorine intercalation compounds (GFIC's) with $3 < nl < 6.4$ exhibit three new lines. These lines have been attributed to off-zone-center phonons rendered Raman-active by the in-plane folding of the Brilouin zone. Electron spectroscopy for chemical analysis and x-ray photoemission spectroscopy[7] measurements of $C_{nl}F(MgF_2)_x$ and $C_{nl}F(HF)_x$ have shown that if $nl > 4$ the C—F bonds are semi-ionic rather than covalent.[8] However, by either heating the compounds or by further increasing the fluorine concentration the C—F bonds change and become covalentlike. The conductivity of the dilute compounds behaves in a way which is typical for acceptor-type graphite intercalation compounds (GIC's);[9] namely, the conductivity increases with fluorine concentration and is followed by a broad maximum in the region $5 < nl < 7$. However, unlike typical GIC's the conductivity drops sharply for $nl < 4$. The conductivity at C_3F is well below the conductivity of the highly oriented pyrolytic graphite (HOPG).[10]

To study the charge transfer in these compounds we have measured the optical reflectivity in the range of 0.8–3.2 eV. The measurements were performed on samples with various fluorine concentrations in the range $3.3 < x < 9.0$. Most of them are found to have a stage-2 structure. The results were interpreted in terms of the two-dimensional (2D) energy-band model suggested by Blinowsky *et al.*[11] Using this model we have estimated the change in the Fermi energy level due to the charge transfer between the fluorine and carbon layers. We shall show that, unlike other GIC's, E_F has a minimum at C_6F which is correlated with the maximum of the conductivity.

This paper is organized as follows: The experimental details and results are presented in the next section. The analysis of the reflectivity spectra and the parameters derived from it are presented in Sec. III. The model for the charge transfer as a function of the in-plane fluorine concentration is discussed in Sec. IV. The work is summarized in the fifth section.

EXPERIMENTAL DETAILS AND RESULTS

GFIC's were prepared[3] by exposing highly oriented pyrolytic graphite (HOPG) to fluorine gas with HF. The GFIC's are very stable and for most experimental studies can be handled in air. The stage index of the samples was characterized with (001) x-ray diffraction. In Fig. 1 we

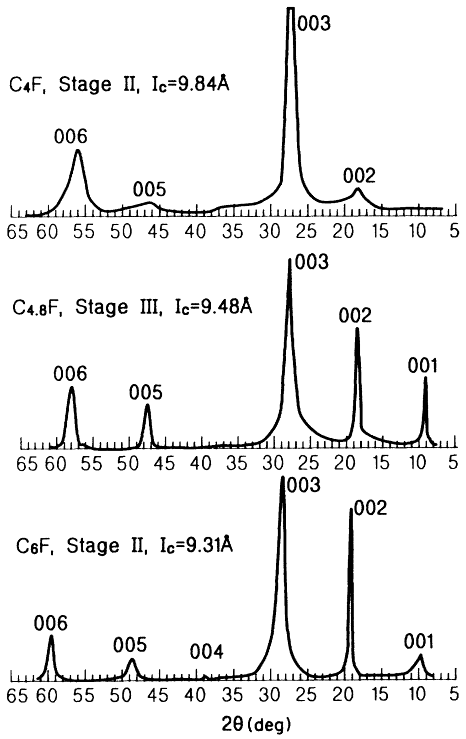

FIG. 1. X-ray diffraction scans (001) of some representative stage-2 compounds.

present some of the x-ray diffraction patterns. The stage index of all the investigated compounds is given in Table I.

The optical reflectivity was measured using a grating monochromator (Perkin Elmer *E*-1) with a tungsten-halogen source. The reflectivity was calibrated by substituting the sample by an Al front mirror and remeasuring the reflectivity. The absolute reflectivity was determined by normalizing the results to the reflection of the 1.96-eV He-Ne laser. Some of the samples were recharacterized by x-ray diffraction after the reflectivity measurements and showed no structural changes.

The optical reflectance spectra were measured on 12 samples with different fluorine concentrations. Most of them were stage-2 compounds, one was a stage 3 and the other were mixtures of either stage 2 and 3 or stage 1 and 2. In Fig. 2 we present three typical reflectivity spectra of $C_{6.7}F$, C_6F, and C_4F. Notice that the energy of the minimum of the reflectivity changes with fluorine concentration. It first increases and has a maximum at 1.36 eV for C_6F. Then it decreases and drops to 1.19 eV for C_4F. The slope of the plasma edge as a function of the fluorine concentration has a similar behavior; namely, the slope is largest for C_6F and it decreases on either side.

ANALYSIS

Using a tight-binding approximation Blinowski *et al.*[11] have calculated the 2D electronic bands for graphite acceptor compounds. The graphite is assumed to be composed of weakly interdependent 2D layers. In stage 1 the energy bands of the Π electrons are linear functions of K, where K is a 2D wave vector,

$$E_{c,v}(K)=\pm\tfrac{3}{2}\gamma_0 bK \ , \tag{1}$$

where $b=1.42$ Å is the nearest-neighbor distance between the carbons and γ_0 is the overlap integral of the Π electrons of neighboring atoms in a single layer. In stage 2 the energy bands of the Π electrons consist of two parallel valence and conduction bands given by

$$\begin{aligned} -E_{v_1}&=E_{c_1}=\tfrac{1}{2}[(\gamma_1^2+9\gamma_0 b^2K^2)^{1/2}-\gamma_1] \ , \\ -E_{v_2}&=E_{c_2}=\tfrac{1}{2}[(\gamma_1^2+9\gamma_0 b^2K^2)^{1/2}+\gamma_1] \ , \end{aligned} \tag{2}$$

γ_1 is the overlap integral of the orbitals of neighboring carbon atoms located on adjacent layers. This overlap splits the conduction and the valence bands. In general, in a stage-n compound there are n conduction and n valence bands located near each corner of the hexagonal Brillouin zone.

The frequency dependent dielectric function has two terms,

$$\epsilon(\omega)=\epsilon^f(\omega)+\epsilon^b(\omega) \ . \tag{3}$$

TABLE I. The parameters obtained from the fit of the experimental reflectivity data with the Blinowsky *et al.* model (Ref. 11).

Sample	Stage index	ω_P^2 (eV)	τ $(\text{eV})^{-1}$	E_F (eV)	f_c	f_m
$C_{9.0}F$	III	11.18±0.17	2.3±0.25			
$C_{8.4}F$	II + III	11.31±0.17	2.6±0.25	0.97±0.015	$0.0192\pm0.5\times10^{-3}$	0.161±0.005
$C_{6.8}F$	II	11.59±0.12	2.8±0.25	0.985±0.01	$0.0198\pm0.4\times10^{-3}$	0.135±0.03
$C_{6.7}F$	II	11.66±0.12	2.4±0.25	0.99±0.01	$0.02\pm0.4\times10^{-3}$	0.135±0.03
$C_{6.0}F$	II	12.03±0.12	4.0±0.25	1.01±0.01	$0.021\pm0.4\times10^{-3}$	0.125±0.003
$C_{5.5}F$	II	11.59±0.12	2.8±0.25	0.985±0.01	$0.0198\pm0.4\times10^{-3}$	0.109±0.002
$C_{5.0}F$	II	11.23±0.17	2.4±0.25	0.97±0.015	$0.0192\pm0.5\times10^{-3}$	0.096±0.003
$C_{4.8}F$	II	10.48±0.17	2.4±0.25	0.915±0.015	$0.0171\pm0.5\times10^{-3}$	0.082±0.003
$C_{4.1}F$	II	9.88±0.23	1.7±0.25	0.88±0.02	$0.0158\pm0.8\times10^{-3}$	0.065±0.003
$C_{4.0}F$	II	9.71±0.23	1.9±0.25	0.87±0.02	$0.0155\pm0.8\times10^{-3}$	0.062±0.03
$C_{3.8}F$	I + II	9.15±0.23	1.8±0.25			
$C_{3.3}F$	I + II	9.03±0.23	1.6±0.25			

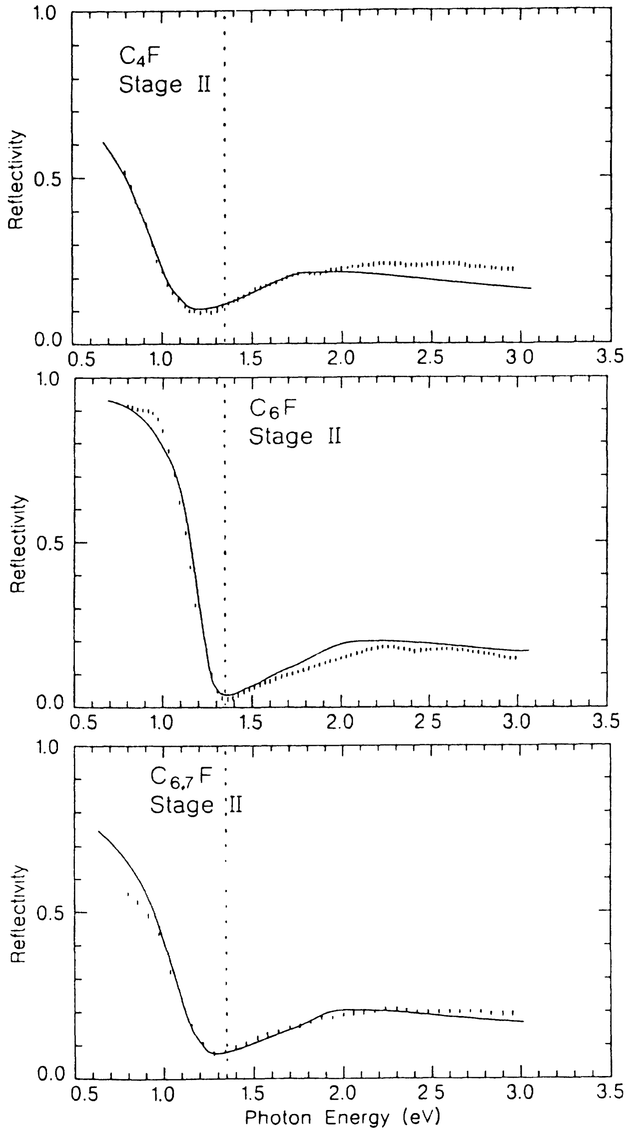

FIG. 2. Representative spectra of the reflectivity measurements. The dots represent the experimental results. The solid lines are the fits using the Blinowski-Rigaux model. Notice that the energy of the reflectivity minimum changes with the fluorine concentration.

The first results from intraband transitions and is described by the Drude expression

$$\epsilon^f(\omega)=\epsilon_\infty[1-\omega_P^2/(\omega^2+i\omega/\tau)] , \tag{4}$$

where $\omega_P,\tau,\epsilon_\infty$ are the plasma frequency, the free-carrier scattering time, and the high-frequency dielectric constant, respectively. The second term has two contributions:

$$\epsilon^b(\omega)=\epsilon^{V\to V}(\omega)+\epsilon^{V\to C}(\omega) . \tag{5}$$

The first describes the contribution from electronic transitions between two valence bands and the second, the contribution from the electronic transitions between the valence and the conduction bands. The different contributions to the real and the imaginary parts of the dielectric function have been calculated by Blinowski *et al.* [Eqs. (27), (30), and (31) in Ref. 11].

The normal reflectance is given by

$$R=\frac{(n-1)^2+k^2}{(n+1)^2+k^2} , \tag{6}$$

where n and k relate to the dielectric function through

$$\mathrm{Re}\epsilon=n^2-k^2,\quad \mathrm{Im}\epsilon=2nk . \tag{7}$$

Whenever $E_F>2\gamma_1$ (the usual case in stages 1 and 2) the reflectance spectra can be divided into three regions: (i) the high-energy region ($\hbar\omega>2E_F$) which is dominated by transitions from valence to conduction bands, (ii) the free-carrier region ($2E_F>\hbar\omega>2\gamma_1$) which includes the plasma edge, and (iii) the low-energy region ($\hbar\omega<2\gamma_1$) which is dominated by the valence-to-valence-band transition term (this term does not exist in stage 1) and the almost total reflection caused by the plasma. The photon energy of the reflectance minimum depends drastically on the Fermi energy through both the intraband term (the plasma frequency) and the interband term (where $2E_F$ is the threshold for the $V\to C$ transition). The slope of the plasma edge defines the free-carrier scattering time but with less accuracy. The plasma frequency, ω_P, and the charge transfer per carbon atom, f_c, depend on the Fermi energy level in the following form:[11]

$$\omega_P^2=\frac{4e^2}{\hbar^2 I_c}E_F,\quad \text{stage 1 ;} \tag{8}$$

$$f_c=f_m/nl=(E_F/\gamma_0)^2/(\sqrt{3}\pi),\quad \text{stage 1 ;} \tag{9}$$

$$\omega_P^2=\frac{8e^2}{\hbar^2 I_c}E_F\left[\frac{E_F^2-\gamma_1^2/2}{E_F^2-\gamma_1^2/4}\right],\quad \text{stage 2 ;} \tag{10}$$

$$f_c=f_m/(2l)=(E_F/\gamma_0)^2(\sqrt{3}\pi),\quad \text{stage 2 .} \tag{11}$$

Here f_m is the charge transfer per intercalated molecule in the compound $C_{nl}X$ (n is the stage index) and I_c is the "c" axis repeat distance. Note that ω_P^2 is proportional to the square root of the charge transfer. This is a direct consequence of the linear dependence of E_F on K near the Fermi level.

The reflectivity measurements (Fig. 2) have been fitted to the above model. In Table I we summarize the fitting parameter values (ω_P,τ) together with the stage index of all the samples. Using Eqs. (10) and (11) we calculated the change in the Fermi energy, the charge transfer per carbon atom, f_c, and the charge transfer per fluorine atom, f_m. In these calculations, the value of γ_0 which represents the in-plane nearest-neighbor interaction was taken to be 3 eV as obtained in Ref. 12. The value of γ_1 was taken to be 0.375 eV.[11,12] Knowing this value accurately is not critical, because a 10% error in the value of γ_1 does not change the results by more than 1%.

The results are given in Table I and are graphically displayed in Figs. 3 and 4, respectively. Notice that ω_P^2 has a rather peculiar behavior as a function of the concentration. It first increases to a maximum at C_6F. Then as the concentration increases further, ω_P^2 decreases

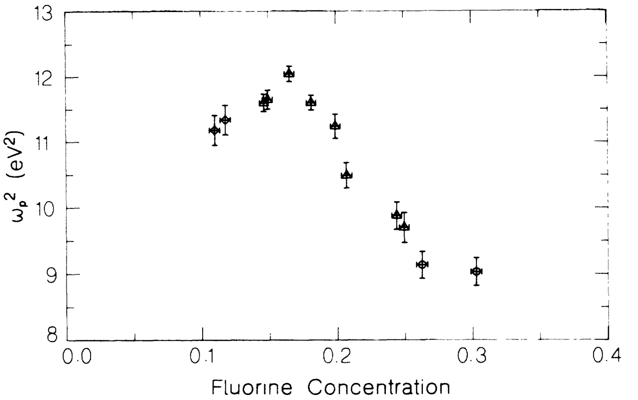

FIG. 3. The square of the plasma frequency as a function of the fluorine concentration. (◇, stage 3; ◇, stage 2 + 3; △, stage 2; and ○ , stage 1 + 2.)

sharply and finally saturates. The charge transfer per fluorine atom has a monotonic decrease as a function of the fluorine concentration. In particular, the value of the charge transfer for C_6F compound is 0.125 electrons per fluorine atom.

DISCUSSION

The maximum in the plasma frequency is unexpected and has not been observed in other GIC's. Usually the plasma frequency increases with intercalant concentration and finally saturates but does not decrease above a certain concentration as in the present case. For example, attempting to increase the total charge transfer beyond that obtained in stage-1 C/AsF_5 (Ref. 13) or stage-1 C/H_2SO_4 (Ref. 14) results in a decrease in the plasma edge slope but does not lead to a lower energy of the minimum of the reflectivity spectrum, as observed in the present case.

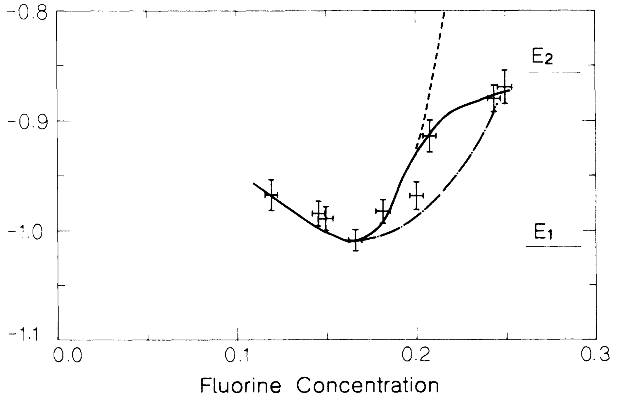

FIG. 4. The Fermi energy E_F as a function of fluorine concentration for stage-2 compounds. The solid line represents the fit using the two-acceptor-stage model. The dashed and the dashed-dotted lines represent model *b* with $A=1$ and $A=0.5$, respectively. This model is in qualitative disagreement with the experimental results.

One of the interesting properties of the fluorine-intercalated graphite is the fact that state 2 exists for a large range of fluorine concentrations from C_8F to C_4F. Consequently, one could expect to be able to treat the charge-transfer problem as a transfer of electrons from the graphite valence bands to an acceptor state E_1. In this case the energy gained by this transfer will be E_F-E_1 per transferred electron. As the concentration increases, the Fermi energy E_F decreases and the charge transfer saturates, if $E_F-E_1 \cong kT$. This approach can then easily explain the saturation of E_F versus the fluorine concentration but not its subsequent increase. The increase in the Fermi energy when the fluorine concentration is increased above C_6F, can be understood in one of two ways.

(i) Beyond C_6F a second acceptor state is created so that with each additional fluorine a total of $A+1$ fluorines are in the new acceptor level reducing the number of fluorines in the first acceptor state by A.

(ii) For each fluorine atom added beyond C_6F, A fluorine atoms in the C_6F compound form covalent bonds with neighboring carbons and the corresponding section of the material becomes essentially insulating. Namely, in that region there are no mobile holes.

The two models can be quantitatively evaluated and compared to the experiment.

Model *a*: From the conservation of the charge for F concentrations smaller than C_6F, we obtain

$$\frac{f_m/2l}{1+\exp[\beta(E_1-E_F)]}=CE_F^2 \quad \text{for } 2l \le 2l_c\ . \tag{12}$$

Here C is taken from Eq. (11) and is equal to $(\sqrt{3}\pi\gamma_0^2)^{-1}$, $2l_c=6$, and $\beta=(kT)^{-1}$. For concentrations larger than C_6F we obtain

$$f_m\left[\frac{(A+1)/2l_c-A/2l}{1+\exp[\beta(E_1-E_F)]}\right.$$

$$\left.+\frac{(A+1)(1/2l-1/2l_c)}{1+\exp[\beta(E_2-E_F)]}\right]=CE_F^2 \quad \text{for } 2l>2l_c\ . \tag{13}$$

Up to the concentration of the C_4F compound, the GFIC's form predominantly stage-2 compounds. Beyond this fluorine concentration, a growing contribution of stage-1 lines shows up in the x-ray diffraction spectra. We interpret this result as an indication that at the fluorine concentration of C_4F the intercalant layer is full. At this fluorine concentration the model requires that all the fluorines must be at the second acceptor state. Namely, the first term in Eq. (11) must vanish. From these considerations we conclude that

$$A=2\ . \tag{14}$$

Equations (12) and (13) can be fitted now to the experimental results in Fig. 4. An excellent fit is obtained with $f_m=\frac{1}{6}$, $E_1=1.034$ eV, and $E_2=0.84$ eV. The corresponding fit of the model to the charge transfer is seen in Fig. 5. Model *b*: The difference between the two models is only in the range $4<2l<6$. According to model *b*, each additional atom together with A atoms which are already present form covalent bonds with carbon atoms rendering a portion of the material insulating. The rest remains essentially in the same state as C_6F. As a result the expression for ω_P^2 given in Eq. (10) should be changed to

$$\omega_P^2=\frac{8e^2}{\hbar^2 I_c}DE_F\left[\frac{E_f^2-\gamma_1^2/2}{E_F^2-\gamma_1^2/4}\right] . \qquad (15)$$

Here D is a relative density factor

$$D=1-A(2l_c/2l-1) \qquad (16)$$

and

$$2l_c=6 .$$

Consequently, the experimental dots in Fig. 4 for fluorine concentrations larger than 0.166 correspond to $E_F'=DE_F$. The theoretical expression for E_F' obtained from the conservation of charge is

$$\frac{1/2l_c}{1+\exp[\beta(E_1-E_F)]}=D^{-2}CE_F'^2 . \qquad (17)$$

This model could not be fitted to the experimental results in Fig. 4. Two examples of the theoretical curves are shown in Fig. 4. The dashed line corresponds to $A=1$ and the dash-dotted line corresponds to $A=0.5$. It is clear that the sharp increase followed by the saturation cannot be reproduced by this model.

The dc conductivity obtained from the measurements of Palchan *et al.*[10] are shown in Fig. 6 together with the ac conductivity calculated from our results. The ac values for fluorine concentrations higher than C_4F are not as accurate as the values for the lower concentrations because the stage is mixed. But they are good enough for the following comments. Allowing for the large scatter in the dc results the two fit reasonably well in the range between C_8F and C_4F. At higher fluourine concentrations the two results completely disagree. This can be understood if we assume that beyond the C_4F concentrations an increasing number of covalent bonds are formed. If the number of these bonds is large enough, the dc conductivity will be greatly reduced and the sample will become insulating below the percolation point. In contrast, the ac conductivity will also decrease but not as much because the insulating parts will be short circuited by the capacitance of the insulating regions. Therefore, these considerations support the suggestion that covalent bonds form at concentrations higher than C_4F.

SUMMARY

In this paper we have presented reflectivity measurements on $C_{2l}F$ compounds with different fluorine concentrations. From the reflectivity spectra we obtained information on the Fermi energy, the charge transfer, and the scattering times of the holes in these compounds. We conclude that three fluorine concentration ranges can be identified.

(1) Stage-2 compounds with fluorine concentrations smaller than C_6F, have one acceptor state with an energy $E_1=-1.034$ eV. In the limit of low concentrations the charge transfer is $\frac{1}{6}$ electron per fluorine atom.

(2) In the concentration range $4<2l<6$, a second acceptor state is formed at $E_2=-0.84$ eV. Each fluorine

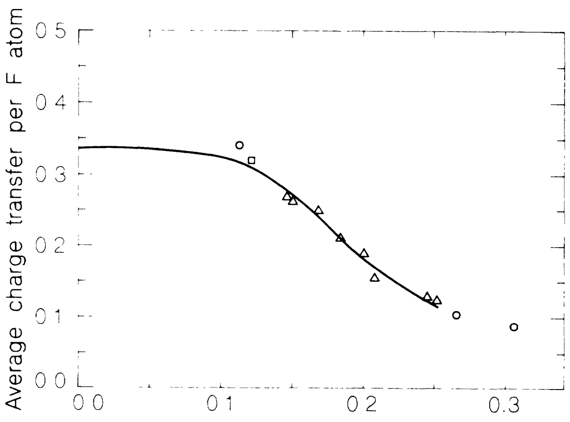

FIG. 5. The average charge transfer per fluorine atom as a function of the concentration. The solid line represents the calculated charge transfer using the two-acceptor-state model. Its extrapolation to low concentrations at stage 2 yields a charge transfer of $\frac{1}{6}$ per fluorine.

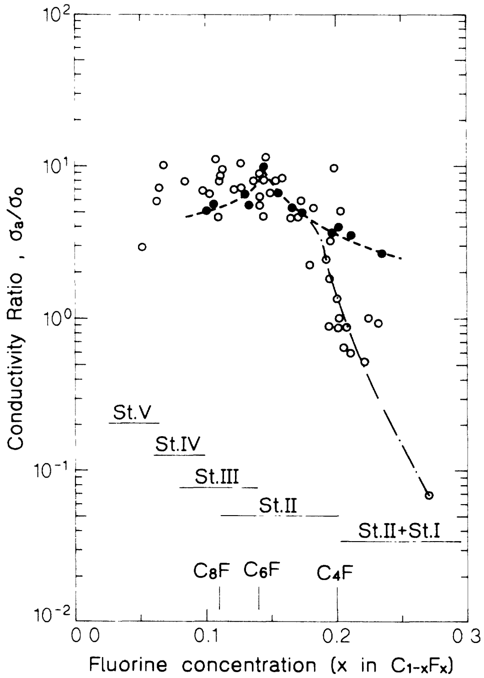

FIG. 6. The optical (solid circles) and dc (open circles) conductivity as function of fluorine concentration. The dashed and the dashed-dotted lines are a guide to the eye. Note that the fluorine concentration in this figure is defined by x in $C_{1-x}F_x$.

which is added above the C_6F concentration transfers two additional fluorines from the E_1 acceptor state to the E_2 state. This results in an increase in the Fermi energy as the concentration increases above C_6F. This result agrees very well with the experimental results. The possibility that in this range, covalent bonds are formed has been considered and discarded.

(3) At concentrations $2l < 4$, it seems that covalent bonds are formed which drastically reduce the conductivity.

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