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IONIC LIMIT IN GRAPHITE-FLUOROARSENATE INTERCALATION COMPOUNDS

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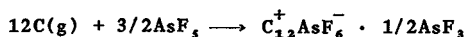
**Naval Research Laboratory, Washington, DC 20375, U.S.A.

Résumé - Les mesures de conductivité électrique, de réflectance et de consommation du fluor suggèrent une limite d'ionisation de C_{20}^+ environ dans les composés de graphite-fluoroarsenate. Une oxydation supérieure à cette limite introduit des centres correspondant à des liaisons covalentes C-F provoquant la diffusion des porteurs ; ceci est déduit des mesures de conductivité en fonction de la température et de XPS.

Abstract - Measurements of electrical conductivity, optical reflectance and F_2 -uptake suggest an ionic limit around C_{20}^+ in graphite-fluoroarsenate compounds. Oxidation beyond this limit introduces carrier scattering centers in the form of covalent C-F bonds as deduced from measurements of conductivity versus temperature and XPS.

INTRODUCTION

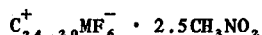
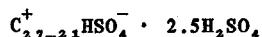
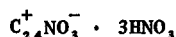
Exposure of graphite to AsF_5 vapor yields intercalation compounds of stoichiometry C_nAsF_6 , where n = stage. Complete oxidation of graphite by AsF_5 is represented by the following reaction:



However, experimental evidence /1/ indicates that only about 40% of the graphite is oxidized in stage 1 and 50% in stage 2. Based on these results, the compositions of stage 1 and stage 2 are



respectively. A charge density of C_{30}^+ for stage 1 is consistent with those values observed in other acceptor-graphite systems. It has been suggested /2/ that neutral spacers are necessary in these materials to screen the intralayer coulomb repulsion between ions. For example, stage 1 compounds having the following compositions have been prepared /3, 4, 5/:



(Prepared using NO_2MF_6/CH_3NO_2 , $M=P, Sb, As$)

The ionic limit in the graphite-bisulfate system has been studied by a series of *in situ* chemical and electronic measurements during electrochemical intercalation /6/. Coulometry and weight uptake measurements show the first

appearance of a stage 1 compound at $C_{21}^+HSO_4^- \cdot 2.5H_2SO_4$. Further oxidation to C_{21}^+ results in enhancement of conductivity and metallic reflectance with no further weight uptake. Charging beyond C_{21} reduces the conductivity, broadens the reflectivity spectrum and introduces C-O covalent bonds. These results suggest that beyond a limiting concentration of HSO_4^- , a covalent guest-host interaction is necessary to overcome coulomb repulsion, and that the C-O bonds introduce a new scattering process which limits the conductivity.

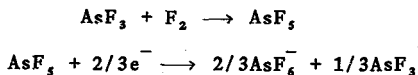
To investigate the ionic limit in the AsF_5 -graphite system, samples were exposed to F_2 to bring about further oxidation of graphite. Our initial qualitative investigation involved *in situ* conductivity and reflectance studies yielding results much like those observed in the graphite-bisulfate system. Tensimetry experiments carried out in conjunction with conductivity measurements were used to determine F_2 uptake at the metallic maximum. Measurements of conductivity versus temperature and C(1s) core level XPS helped to identify the origin of the conductivity decrease.

EXPERIMENTAL

Samples of $C_{80}AsF_5$ were prepared by exposing highly oriented pyrolytic graphite (HOPG) to AsF_5 vapor /7/. These samples were exposed to F_2 at pressures ranging from 1.0 to 1.5 atm. Room-temperature conductivity measurements (basal plane) were made *in situ* using a contactless 1kHz inductive technique /8/. Measurements of conductivity versus temperature were made using a contactless inductively coupled method in which the sample rotates in a magnetic field /9/. Optical reflectance spectra were obtained from an automated single-beam spectrometer /10/. X-ray photoelectron spectra were obtained from a McPherson ESCA 36 photoelectron spectrometer using a $MgK\alpha$ (1253.6eV) X-ray source.

RESULTS

The increase in conductivity (Figure 1) and blue shift of the plasma edge (Figures 2 and 3) observed during initial exposure of $C_{80}AsF_5$ ($n=1,2$) to F_2 , imply an increase in free carrier concentration due to further production of AsF_6^- . The subsequent decrease in conductivity and broadening of the edge suggest a reduction in carrier scattering time. This is confirmed by the changes that occur in $\alpha_a(T)$ (Figure 4) upon fluorination and the formation of covalent C-F bonds as determined by XPS (Figure 5). Tensimetry data (Table I) suggest a charge density of C_{20}^+ at the metallic maximum based on the reaction sequence



CONCLUSIONS

The effect of fluorine on the electrical and optical properties of $C_{80}AsF_5$, suggest the existence of an ionic limit at C_{20}^+ . Beyond this limit direct fluorination of the graphite lattice occurs, limiting the conductivity via defect scattering. The similarities between the AsF_5 -graphite system and other acceptor-graphite systems, particularly the bisulfate-graphite system, imply that all acceptor intercalants give the same conductivity.

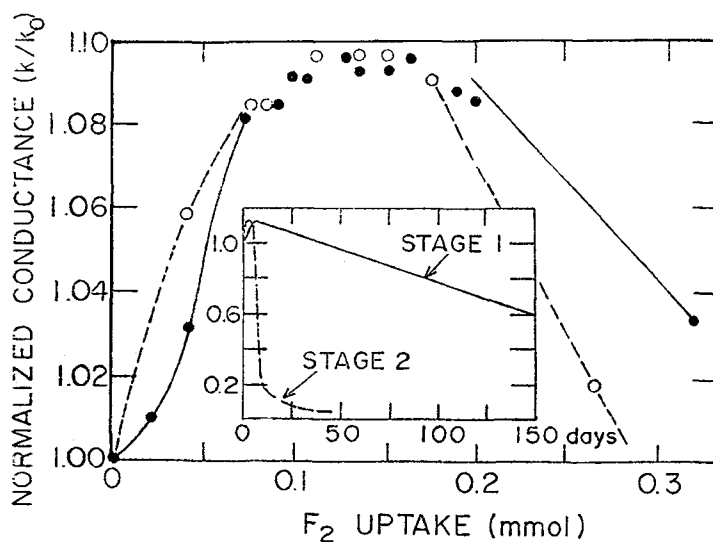


Figure 1: Conductance per C layer versus F_2 uptake (main figure) and versus time of exposure to ~ 1 atm F_2 (inset). Values normalized to the starting materials $C_{24}AsF_6$. Filled circles and solid curve for stage 1, open circles and dashed curve for stage 2, corresponding to samples C and E in Table I. Note that k/k_0 first increases by 10% then drops to below the pure graphite values ($k/k_0 = 0.1$ for HOPG).

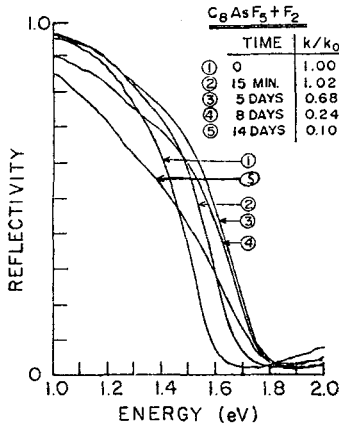


Fig. 2: Reflectivity spectra recorded after various times of F_2 exposure for initially C_8AsF_5 . The small initial blue shift of the metallic edge (curves 1-3) and the eventual broadening (curve 5) correlate with the initial increase followed by a decrease of k/k_0 in Fig. 1.

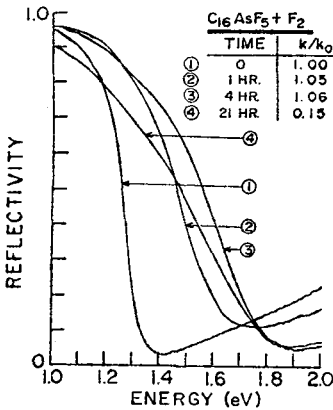


Fig. 3: Similar to Fig. 2 for initially $C_{16}AsF_5$. The large blue shift from curves 1 to 3 correlates with a stage change from 2 to 1.

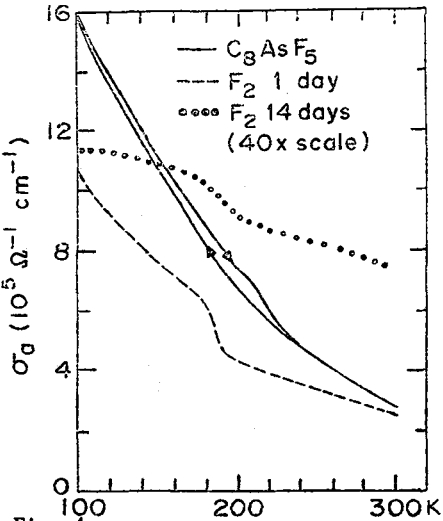


Fig. 4: Temperature dependent basal plane conductivity of C_8AsF_5 after 0, 1 and 14 days F_2 exposure (solid, dashed and dotted curves respectively). Note the scale change for the highly fluorinated (poorly conducting) sample.

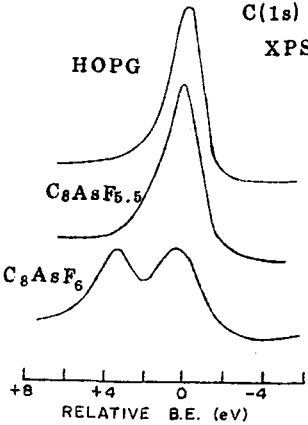


Fig. 5: C(1s) core level XPS spectra for HOPG, lightly and heavily fluorinated C_8AsF_6 .

		STAGE I			STAGE 2		
		A	B	C	D	E	
1.	carbon	4.01	4.80	5.39	4.13	5.31	
2.	AsF ₅ equiv.	0.501	0.600	0.674	0.258	0.332	
3.	AsF ₆ ⁻	BARTLETT	0.334	0.400	0.449	0.172	0.221
4.	AsF ₃		0.167	0.200	0.225	0.086	0.111
5.	AsF ₆ ⁻	MORAN	0.134	0.160	0.180	0.090	0.116
6.	AsF ₃		0.067	0.080	0.090	0.045	0.058
7.	AsF ₅		0.301	0.360	0.407	0.122	0.157
8.	F ₂ at k(max)		0.10	0.13	0.14	0.12	0.14
9.	new AsF ₆ ⁻		0.067	.087	.093	0.08/ 0.16	0.09/ 0.19
10.	carbon charge		C ₂₀ ⁺	C ₁₉ ⁺	C ₂₀ ⁺	C ₁₆ ⁺ / C ₂₄ ⁺	C ₁₇ ⁺ / C ₂₅ ⁺
11.	Approx. final composition		C ₈ AsF ₆			C ₈ AsF ₈₋₉	

Table I: Analysis of fluorine tensimetry data. Rows 1-2 characterize the initial compounds assuming C₈AsF₆ overall composition (all quantities in mmol.) Rows 3 and 4 give the species present according to Bartlett /11/, while the alternative situation in rows 5-7 results from the conclusions of Moran. Row 8 is the F₂ uptake at the conductance maximum (i.e. Fig. 1) while rows 9 and 10 give the increase in ion concentration and carbon charge based on rows 5-7. The last row gives the final composition after F₂ uptake has essentially stopped.

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