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Author

Thompson, Thomas E.

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Thomas E. Thompson, Eugene M. McCarron, and
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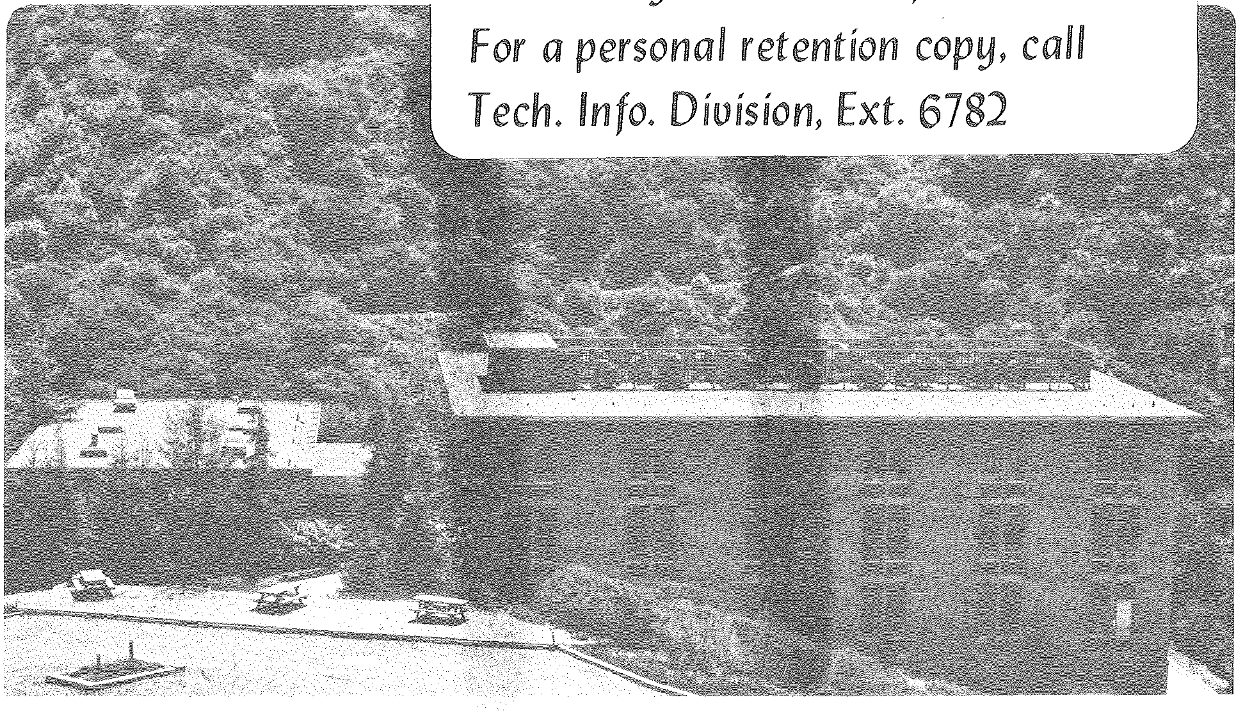

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THE ELECTRICAL CONDUCTIVITY OF GRAPHITE-AsF_5 INTERCALATION COMPOUNDS AND THEIR RELATIONSHIP TO OTHER GRAPHITE-MF_6 SALTS

Thomas E. Thompson
SRI International, Menlo Park, California 94025 (USA)

Eugene M. McCarron and Neil Bartlett
Department of Chemistry, University of California and
Lawrence Berkeley Laboratory, Berkeley, California 94720 (USA)

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Summary

The relationship between the electrical conductivities and the chemistry of graphite-AsF_5 compounds has been investigated. Comparisons are made with graphite$^+$-AsF_6^- relatives and with graphite compounds of the third-series transition metal fluorides. The room-temperature, basal-plane conductivity of $C_{8\underline{n}}AsF_5$ is found to be approximately independent of stage for $\underline{n} = 1$ to 3, with a range of values ±12% about a mean value of 2.9×10^5 $(\Omega\text{-cm})^{-1}$-- approximately half the value for copper.

The chemistry of $C_{8n}AsF_5$ for $\underline{n} \geq 2$ is dominated by the disproportionation of the AsF_5 molecule and the oxidation of the graphite according to $2e^- + 3AsF_5 \rightarrow 2AsF_6^- + AsF_3$. For second- and higher-stage materials, AsF_3 can be removed and added back again to the graphite compound without significant change in the conductivity. Second- and higher-stage graphite-AsF_6 salts, $C_{12\underline{n}}AsF_6$ ($\underline{n} \geq 2$), also have conductivities comparable to those of their $C_{8\underline{n}}AsF_5$ relatives of the same stage. In the first-stage salt, which has a composition range $C_{12}AsF_6$ to C_8AsF_6, basal-plane conductivities are approximately an order of magnitude lower than in the second- and third-stage salts. Fluorination of $C_{8\underline{n}}AsF_5$ materials generates AsF_6^- salts, but such salts usually incorporate extra fluorine to a limiting corporation $C_{\underline{x}}AsF_6 \cdot \frac{1}{2} F_2$. These fluorine-rich systems have lower basal-plane conductivities than do their $C_{\underline{x}}AsF_6$ relatives.

1. Introduction

Since the first reports [1,2] that the room-temperature, basal-plane conductivities of certain graphite-AsF_5 intercalation compounds are of the same magnitude as the conductivity of copper, efforts [3-6] to reproduce these results have been unsuccessful. In fact, recent measurements of the conductivities of the graphite-AsF_5 compounds consistently give values that are only half that of copper, as shown in Fig. 1. The inconsistency of these results raises questions about both the techniques employed to measure the conductivity and the methods used to prepare and characterize the samples. This paper emphasizes the relationship between the conductivity and the chemistry of the graphite-AsF_5 compounds and their AsF_6^--salt relatives.

There has been much discussion concerning the validity of the claims of Bartlett *et al*. [7,8] that the intercalation of AsF_5 into graphite involved conversion of AsF_5 to AsF_6^- and AsF_3 according to the equation

$$3AsF_5 + 2e^- \rightarrow 2AsF_6^- + AsF_3 \qquad (1)$$

Recently, McCarron and Bartlett [9] have shown that graphite$^+$-AsF_6^- salts obey a staging formula $C_{12\underline{n}}AsF_6$ for stages of 2 or higher and that addition of AsF_3 converts such a salt to its $C_{8\underline{n}}AsF_5$ relative:

$$C_{12\underline{n}}AsF_6(s) + \frac{1}{2}\,AsF_3(g) \rightarrow C_{12\underline{n}}AsF_6 \cdot \frac{1}{2}\,AsF_3(s) = \frac{3}{2}\,C_{8\underline{n}}AsF_5(s) \qquad (2)$$

Conversely, $C_{8\underline{n}}AsF_5$ under vacuum loses AsF_5 and AsF_3, but AsF_3 is the dominant volatile for $\underline{n} \geq 2$:

$$\frac{3}{2}\, C_{8\underline{n}}AsF_5(s) \rightarrow C_{12\underline{n}}AsF_6(c) + AsF_3(g). \qquad (3)$$

Thus, loss of AsF_3 from graphite-AsF_5 produces a graphite$^+$-AsF_6^- salt, and addition of AsF_3 to the latter produces the former. These interconversions occur without change in stage. Loss of AsF_5, on the other hand, which occurs in stage-1 material and to some extent in stage-2 material, does lead to higher-stage material.

In this study, we compare the basal plane conductivities of the AsF_5- and AsF_6-graphite materials related through eqns. (2) and (3) as well as of material produced by treating AsF_5-graphite with fluorine.

2. Experimental

2.1 Synthesis and Conductivity of AsF_5 Compounds

Graphite-AsF_5 samples for conductivity measurements were made by treating highly oriented pyrolytic graphite (HOPG) (Union Carbide) with from 300 to 2000 torr of AsF_5 gas at room temperature. The preparation techniques and characterization methods were essentially the same as those described by Falardeau *et al.* [10]. The HOPG was cut by air abrasion into square plates, typically 5 × 5 mm^2, with the plane of the plate perpendicular to the c-axis. The plates were cleaved to a typical thickness of 0.5 mm. Prior to the reaction, the HOPG and the reaction vessel (made of Pyrex® or quartz with passivated 316 stainless steel or Monel® fittings and valves) were thoroughly dried by vacuum baking or prefluorination. The AsF_5 (Ozark-Mahoning) was purified by trap-to-trap distillation. Infrared spectroscopy showed that other infrared-active components were absent from the distillate. The facile loss of AsF_3 from low-stage graphite-AsF_5 causes uncertainty concerning the composition of materials previously described as $C_{\underline{x}}AsF_5$, since such loss requires AsF_6^- salt generation, as in eqn. (3). This is of particular concern where researchers have terminated reactions by pumping out the volatiles from the reaction vessel held at room temperature. All of our samples were transferred to dry nitrogen, with care taken not to subject them to vacuum. They were subsequently handled in a dry box (Vacuum Atmospheres Corp. Drilab). Stage and composition were determined by X-ray diffraction and by direct weight and thickness measurements in the dry box. X-ray analysis and gravimetry correlated well, as has been reported earlier [9,10]; however, for stages 2 through 5 the measured thicknesses were systematically 5% larger than those given by the theoretical expression $\underline{t}/\underline{t}_o = [8.05\ \text{Å} + (\underline{n} - 1)3.35\ \text{Å}]/\underline{n}(3.35\ \text{Å})$. One first-stage compound was 16% over the theoretical value because of exfoliation.

Room-temperature, basal-plane conductivity measurements were made in situ as AsF_5 intercalation of the HOPG proceeded. A commercial contactless-conductivity apparatus (Arnatronics F.O.M. 7734) described in detail in an earlier publication [3] was employed for these measurements. The 1-kHz induction field of our apparatus eliminated skin-depth problems, which are known to arise when this contactless method is used with graphite compounds at higher frequencies [5]. The apparatus produces an output voltage $V \propto \sigma \underline{S}^2 \underline{t}$, where σ is the average basal plane conductivity, $\underline{S}$ is the area of the sample, and $\underline{t}$ the thickness. For absolute conductivity determinations the constant of proportionality is determined with copper pieces of size and shape similar to the HOPG samples.

The gravimetric composition, thickness ratios, oscillator voltage ratio, and the ratio of conductivity to that of the starting graphite, $\sigma/\sigma_G = V/V_o \times \left(t/t_o\right)^{-1}$, are presented in Table 1. It is not clear how the observed systematic error ($\sim$5%) in the thickness should be considered in the error analysis of σ/σ_G. If the increase is related to a distribution of microscopic cracks that are smaller than the skin depth of the electromagnetic field, no correction should be made in σ/σ_G. On the other hand, if the increased thickness is related to cracks that produce layers of macroscopic void, a correction should be applied. In any case, the values of σ/σ_G are not known to better than 10%. The absolute conductivity values indicated in Fig. 1 are based on a primitive HOPG value $\sigma_G = 2.5 \times 10^4 (\Omega\text{-cm})^{-1}$: All of our starting graphite was within 8% of this value. The range of values in Fig. 1, the first ten samples in Table 1, is ±12% about a mean value of 2.9×10^5 $(\Omega\text{-cm})^{-1}$, approximately half that of copper.

2.2 Removal of Volatiles from HOPG-AsF_5

A preliminary description of the nature of the volatiles removed at room temperature from $C_{8\underline{n}}AsF_5$ as a function of stage and pumping time has been given [9], and a full account will appear elsewhere [11]. Within the first minute, stage-1 material yields predominantly AsF_5 with some AsF_3. As the composition approaches $C_{10}AsF_{5-6}$, the ratio of AsF_3 to AsF_5 becomes approximately 1:1, and this proportion increases rapidly beyond that composition. At second stage, the volatiles are predominantly

AsF_3, initially accompanied by AsF_5. For stage 3 and higher, AsF_3 has been the only detectable volatile at 25°C. Heating will produce AsF_5 in the higher-stage compounds; for example, at 100°C AsF_5 is evolved from a stage-4 sample, but AsF_3 still dominates.

As mentioned earlier, loss of AsF_3 from graphite-AsF_5 produces a graphite-AsF_6 salt, but addition of AsF_3 to the AsF_6 salt produces the AsF_5 compound. Table 2 presents the gravimetric composition, thickness ratios, and conductivity ratios ($\sigma/\sigma_o = \left(\underline{t}/\underline{t}_o\right)^{-1} \times V/V_o$) for four separate samples that were alternately pumped and treated with AsF_3. Pumping times varied from 24 hours to several days. The AsF_3 was prepared by the reduction of AsF_5 gas with an excess of arsenic metal and characterized by infrared absorption. Reactions with AsF_3 were in the vapor at room temperature and were allowed a minimum of 12 hours. Thickness and weight determinations were made directly on the samples by removing them from the reaction vessel in the nitrogen-filled dry box. The reproducibility of the data in Table 2 was found to be ±0.05 for $\underline{t}/\underline{t}_o$ and ±0.7 for σ/σ_G.

If only AsF_3 were removed from $C_{\underline{x}}AsF_5$ according to eqn (3), the resulting material after sufficient pumping time would be $C_{3\underline{x}/2}\ AsF_6$. Furthermore, the reversibility of the process according to eqn. (2) would produce the same $C_{\underline{x}}AsF_5$ if the reaction were to proceed to completion. Although for second and higher stages the fraction of the volatile material that is AsF_5 is always lower than AsF_3, there must always be some AsF_5 removed. Such an effect appears to be indicated by the observation of a small decrease in arsenic content in the $C_{\underline{x}}AsF_5$ samples along with a small decrease in thickness ratio, $\underline{t}/\underline{t}_o$, over long time periods. This is, of course, consistent with the equilibrium

$$3AsF_5 + 2e^- \rightleftarrows 2AsF_6^- + AsF_3. \qquad (4)$$

The data in Table 2 also show that there is a small systematic decrease in the conductivities of the HOPG compounds $C_{8\underline{n}}AsF_5$ and $C_{12\underline{n}}AsF_6$ throughout the series of interconversions. This effect could also be caused solely by the loss of AsF_5.

2.3 HOPG-AsF_6 Prepared by Reaction with $O_2^+AsF_6^-$

Graphite-AsF_6 salts were also prepared by treating HOPG with O_2AsF_6 [11]. One sample was prepared in a mixture of $SO_2C\ell F$ and O_2AsF_6 held at -60°C for three days. This sample split into five pieces. Another HOPG sample was buried in an excess of O_2AsF_6 powder for 21 days. Whether the $O_2^+AsF_6^-$ interacts with the graphite by route (a) or (b):

(a) $O_2^+AsF_6^- + \text{graphite} \rightarrow \text{graphite}^+\text{-}AsF_6^- + O_2$

(b) $O_2AsF_6 \rightleftarrows O_2F + AsF_5$

$O_2F + AsF_5 + \text{graphite} \rightarrow \text{graphite}^+\text{-}AsF_6^- + O_2$,

the outcome of the reaction must be an AsF_6^- salt, unless in (b) O_2F is consumed by interactions with impurities or the container. In those circumstances, which we believe do not obtain in our work, the product would be intermediate between $C_{\underline{x}}AsF_6$ and $C_{\underline{x}}AsF_5$. The results of gravimetry, thickness measurements, and contactless-conductivity measurements are presented in Table 3. For the sample that split into five pieces, weight and thickness determination was made from the sum of all five pieces, and conductivity was measured five times. Note that the mixed stage-2/stage-3 material has conductivities similar to the HOPG-AsF_5 compounds, whereas the predominantly stage-1 AsF_6 material has a greatly reduced conductivity.

2.4 Addition of F_2 to HOPG-AsF_5

HOPG-AsF_5 samples were treated with F_2 at pressures near 1500 torr for 24 hours to produce AsF_6 salts. A comparison of composition, thickness, and conductivity of these materials, before and after treatment, is presented in Table 4.

We remarked earlier on the accuracy of thickness and conductivity measurements. Only in Table 4 does the uncertainty in gravimetry become significant. Weights were measured to ±0.5 mg; the starting graphite samples weighed approximately 30 mg. The most significant uncertainty occurred for sample 13, where the upper limit of composition after reaction could be $C_{40.4}AsF_6 \cdot 0.6F_2$ if some of the weights are modified by 0.1 mg.

Several significant facts are observed in Table 4: little or no reaction occurred with the stage-1 HOPG-AsF_5 sample; the mixed stage-1/stage-2 AsF_5 sample reacted with the F_2 in proportion to its stage-2 content; the $C_{12\underline{n}}AsF_6$ salts take up excess F_2 for $\underline{n} \geq 2$; $\underline{t}/\underline{t}_o$ increases for all the reacted material; and the conductivities of all the compounds that reacted are significantly reduced.

The lack of reaction with the stage-1 AsF_5 compound was unexpected. We were finally able to produce a reduction in the conductivity after extended pumping on the sample and adding F_2, but (of course) this produced a higher-stage material of unknown composition. This lack of reaction until after pumping was observed for two separate samples.

From gravimetry data we observe that fifth-stage $C_{39.7}AsF_6$ takes up an extra half mole of fluorine, as reported earlier [9]. First-stage $C_{12}AsF_6$ does not take up extra fluorine; thus $C_{18.6}AsF_6$, which is approximately a 1:1 mix of $C_{12}AsF_6$ and $C_{24}AsF_6$, takes up approximately 1/4 mole F_2, since the limiting composition of the second-stage material is $C_{24}AsF_6 \cdot \frac{1}{2} F_2$. The observed product of $C_{12.7}AsF_5 + \underline{x}F_2$ is completely consistent with the fact that 41% of the starting material is C_8AsF_5, which is expected to have little or no reaction with the fluorine.

The observation that the thickness of the $C_{8\underline{n}}AsF_5$ samples increases upon treating with F_2 is consistent with the less-dense packing of the galleries of the AsF_6 salts, according to the staging formula $C_{12\underline{n}}AsF_6$. For instance, stage-3 $C_{24}AsF_5$ is thinner than stage-2 $C_{24}AsF_6$. However, the observed thickness ratios after treatment for samples 7 and 13 exceed the values 2.03 and 1.53, respectively, which are predicted by theory:

$$(\underline{t}/\underline{t}_o)_{after} = 3/2[(\underline{t}/\underline{t}_o)_{before} - 1/3].$$

As a further check of our understanding of the chemistry of these compounds, excess AsF_3 was added to the fluorinated sample 13 (Table 1),

$C_{39.7}AsF_6 \cdot 0.5F_2$. It was calculated that 4.9 mg of AsF_3 was needed to achieve a complete reduction of the AsF_6 and $0.5F_2$. The measured uptake of 5.0 mg was easily within the experimental uncertainty to produce $C_{19.5}AsF_5$. The thickness, oscillator voltage, and conductivity ratios for this reaction are shown in Table 5. The increases in thickness are consistent with going from an HOPG-AsF_6 compound, which is a mixture of stage 3 and 4, to an AsF_5 compound, which is a mixture of stage 2 and 3.

The increase in conductivity produced by this titration indicates that the excess F_2 in the AsF_6 compound is reducing the conductivity. The data in Tables 1-5 clearly indicate that stage-1 HOPG-AsF_6 and the higher-stage HOPG-AsF_6 materials that contain F_2 have conductivities considerably lower than either HOPG-AsF_5 compounds or higher-stage HOPG-AsF_6 compounds that contain no F_2. This will be discussed fully in the next section.

3. Discussion and Conclusions

Our measured values for the basal-plane conductivities of HOPG-AsF_5, given in Fig. 1 and Table 1, are in very good agreement with those determined by at least three other groups [4-6]. They also agree with earlier unpublished values [13] determined from dc measurements on bridge samples. Since several different measurement techniques and apparatus were used (a resonant 1-kHz oscillator employing a ferrite-core coil [3], an air core transformer with frequencies from 0.6 to 30 kHz [4], a mutual induction technique with coils on opposite sides of the sample [4], and a 1-kHz Wien induction bridge oscillator [6]), this agreement indicates that a fundamental property of the material is being measured. Our mean value for the room-temperature basal-plane conductivity of $C_{8\underline{n}}AsF_5$ for $\underline{n}$ = 1,2, or 3 is 2.9×10^5 (Ω-cm). This value is approximately half that determined by earlier 100-kHz contactless measurements [1,2], which are now believed to be in error because of problems associated with the limited penetration of the 100-kHz electromagnetic fields [5].

The conductivity σ in Fig. 1 and Table 1, which represents the conductance of a unit cross-sectional area and a unit length of bulk HOPG-AsF_5, is useful from an engineering viewpoint. We would ultimately like to understand the microscopic conduction processes in terms of the local charge density and scattering mechanisms. We would like to know the profile of the microscopic conductivity along the c-axis of the sample. For the AsF_5 compounds, it is easy to calculate the average of the microscopic conductivity throughout the carbon layers themselves, because the conductance of the AsF_5 layers can be safely assumed to be negligible, as evidenced by the extremely high anisotropy of the conductivity tensor [2]. Since all evidence indicates that the thickness of the carbon sheets does not change significantly upon intercalation--but rather the sample expands because of insertion of AsF_5 layers--the fraction of the HOPG-AsF_5 sample that is conducting carbon is $\underline{t}_o/\underline{t}$, and the average conductivity of the carbon layers is given by $\sigma\underline{t}/\underline{t}_o$. Conveniently, the ratio of the average carbon-layer conductivities before and after intercalation, K/K_G, is simply related to the voltage of our measuring apparatus: $K/K_G = (\sigma/\sigma_G) \times (\underline{t}/\underline{t}_o) = V/V_o$. Since the thickness of the carbon sheets does not change, K/K_G is also the conductance ratio.

Fig. 2 illustrates the average carbon-layer conductivity ratio K/K_G ($= V/V_o$) for cases where series of measurements were made on three separate samples as each sample progressed through different stages. These data include an extensive set from the work of Interrante, Markiewicz, and McKee [4]. From this plot we can draw two conclusions: $K/K_G \propto 1/\underline{n}$ for $2 \leq \underline{n} \leq 10$; and there is a sharp break in the slope of the linear dependence of K/K_G as a function of $1/\underline{n}$ between second- and first-stage.

We can analyze the $1/\underline{n}$ dependence of K in terms of the currently emerging theoretical picture that electronic screening of the intercalant ions must localize most of the mobile electronic charge to just a few carbon sheets on either side of the intercalated gallery [14]. In a simplified version of this picture, we will consider that there are $\underline{m}$ high-conductivity carbon sheets with conductivity $\sigma_{\underline{h}}$ on each side of an intercalated gallery, and that the remaining carbon sheets have a conductivity $\sigma_{\underline{\ell}}$, which is presumably much lower. This scheme is shown in Fig. 3. In this picture the charge profile and scattering mechanisms in the high conductivity carbon sheets are independent of stage, $\underline{n}$, to to point where these sheets overlap. The conductance of the $\underline{n}$ carbon sheets is the sum of the conductances from the $2\underline{m}$ highly conducting carbon sheets and the contribution from the $(\underline{n} - 2\underline{m})$ low-conductivity sheets. The conductance relative to that of the starting graphite is thus:

$$K/K_G = [2\underline{m}\sigma_{\underline{h}} + (\underline{n} - 2\underline{m})\sigma_{\underline{\ell}}]/\underline{n}\sigma_G$$

$$= \sigma_{\underline{\ell}}/\sigma_G + 2m(\sigma_{\underline{h}} - \sigma_{\underline{\ell}})/\sigma_G \times (1/\underline{n}). \qquad (5)$$

For large $\underline{n}$ we expect that $\sigma_{\underline{\ell}} \approx \sigma_G$. The linear least-square fit to the data in Fig. 2 gives $K/K_G = (-0.4 \pm 1.1) + (46.5 \pm 3.6)/\underline{n}$, indicating $\sigma_{\underline{\ell}} < \sigma_G$ for $\underline{n} = 2$ through 10. The linearity of K up to $\underline{n} = 2$ indicates that the boundary layers do not interfere until $\underline{n} = 2$. We interpret this by choosing $\underline{m} = 1$, for which case $\sigma_{\underline{h}}/\sigma_G = 23 \pm 2$.

As discussed, the investigations of McCarron and Bartlett [9] have shown that for second and higher stage, the equilibrium of eqn. 4 is far to the right; such graphite-AsF_5 compounds are largely represented by the formula $C^+_{12\underline{n}}AsF^-_6 \cdot \frac{1}{2} AsF_3$ ($\underline{n} \geq 2$). While the AsF_3 can be removed by pumping, the AsF^-_6 is difficult to remove. In this study we have seen that the electrical conductivity of these same compounds is changed little, if at all, with the removal of AsF_3 (Table 2); furthermore, the conductivity of a mixed stage-2/stage-3 HOPG-AsF_6 sample is similar to that of HOPG-AsF_5 material. (The presence of unreacted AsF_5 molecules in the compounds is clearly of secondary importance for $\underline{n} \geq 2$.) Thus, we may conclude that the conductivities of second- and higher-stage HOPG-AsF_5 compounds are determined by the AsF^-_6 ions.

From the linear fit to the data in Fig. 2, we can test the ratio of the number of mobile holes in the carbon sheets to the number of intercalated AsF_5 molecules, usually designated as $\underline{f}$. If each AsF^-_6 ion is associated with one hole, the value for $\underline{f}$ will be 2/3. For the compound $C_{8\underline{n}}AsF_5$ the density of holes, $\underline{p}$, is given by:

$$p = (n/2m) \times f \times (d_c/8n), \qquad (6)$$

where $2m/n$ is the fraction of the carbon sheets that receive the charge, and d_c is the density of carbon atoms, which equals 1.14×10^{23} cm^{-1}. Using eqn. (6) with the conductivity value found from Fig. 2, $\sigma_h = 23\sigma_G/m$, and assuming a single carrier picture for the conductivity, we can determine a mobility, $\mu = \sigma_h/pe = (1/f) \times 500$ $\mathrm{cm}^2/\mathrm{V\ s}$. A value of $f = 2/3$ leads to a mobility of 750 $\mathrm{cm}^2/\mathrm{V\ s}$, which is quite reasonable when compared with recent experimental results [15].

The break in conductance between stage-2 and stage-1 seen in Fig. 2 is not surprising, since in the stage-1 material each carbon sheet is sandwiched between two galleries of intercalant anions. There must be a good deal more scattering of the electrons for such a configuration, and hence a reduced mobility, as well as the opportunity for greater charge localization than in the higher stages. However, the ease with which AsF_5 can be removed from the stage-1 compound leads one to question whether the galleries also contain unreacted AsF_5 molecules. Such neutral species, along with the neutral AsF_3 molecules, would have a tendency to minimize the effects of charge localization and scattering mentioned above. We can put an upper limit on the fraction of un-ionized AsF_5 in the galleries of the stage-1 material by assuming that this material has the same mobility as the higher-stage materials and that the carrier density is proportional to the number of AsF_6^- ions, as in the cases for $n \geq 2$. If the conversion represented in eqn. (1) is essentially complete for all stages in the linear region of Fig. 2, the fact that the stage-1 conductance ratio of 30 is 64% of the value found from extrapolating the linear data to $\underline{n} = 1$ implies that the amount of un-ionized AsF_5 is 36%. This is, of course, an upper limit: Note that in this limit the material would be $C_8^{-0.43}(AsF_6^+)_{0.43}(AsF_3)_{0.21}(AsF_5)_{0.36}$.

It will be noted (see Table 3) that the largely first-stage material $C_{14}AsF_6$ made by interaction of $O_2^+AsF_6^-$ with graphite is a poor conductor (approximately 5 times graphite) whereas the mixed second- and third-stage material has a conductivity similar to that of second- or third-stage $C_{8\underline{n}}AsF_5$. We have noted a similar dramatic decrease in conductivity, with increase in charge, in passing from second- to first-stage material in the salts $C_{\underline{x}}^+MF_6^-$ (M = Ir,Os) [3]. We might, therefore, have expected the conductivity of C_8AsF_5 to be even lower than observed, particularly if the conversion of AsF_5 to AsF_6^- according to eqn. (1) were complete. That it is a better conductor than expected on this basis may result from interference of the neutral molecules (AsF_3 and AsF_5) with the charge cooperativity noted above.

Fluorination of $C_{8\underline{n}}AsF_5$ brings about a change in stage for all but the first stage. Whereas fluorination of the stage-1 AsF_5 compounds appears not to take up fluorine beyond $C_{12}AsF_6$, there is usually an excess fluorine uptake in the second- and higher-stage $C_{12\underline{n}}AsF_6$ salts, with a limit set at $C_{12\underline{n}}AsF_6 \cdot \frac{1}{2} F_2$, as can be seen in Table 4. We have been concerned to determine the nature of this extra fluorine and its impact upon the conductivity.

The fluorination of the HOPG-AsF_5 material $C_{39.7}AsF_5$ produces a significantly poorer conductor (see Table 4). This material, when treated with excess AsF_3, undergoes conversion to $C_{19.5}AsF_5$ according to the idealized equation

$$C_{40}AsF_6\cdot\frac{1}{2}\,F_2 + AsF_3 \rightarrow 2C_{20}AsF_5 \ . \qquad (7)$$

There is no doubt that the extra F_2 incorporated by C_xAsF_6 is available to oxidize AsF_3. It seems likely, therefore, that the extra fluorine is entering the hexagonal vacancies in the $C_{12}^{+}AsF_6^{-}$ anion array as two fluoride ions. The "extra" fluorine cannot be pumped out at ordinary temperatures, and paramagnetic species such as F_2^{-} have been ruled out by magnetic susceptibility measurements [16]. We are led to surmise that the two F^{-} ions per AsF_6^{-} packing vancancy (see ref. 8) are each placed at the poles of the vacancy, such that each F^{-} is in close contact with an adjacent carbon sheet. The formation of C-F covalent bonds would require tetrahedrally bonded carbon atoms, which would cause warping of the graphite sheets. The loss of resonance energy attendant upon such a structural change would surely be great. The charge enhancement that our model requires is large; the average carbon atom charge in $C_{12n}^{2+}AsF_6^{-}F^{-}$ is double that in $C_{12n}^{+}AsF_6^{-}$. Also, note that second-stage $C_{24}^{2+}AsF_6F^{-}$ has the same carbon charge as $C_{12}^{+}AsF_6^{-}$, which is known to be a poor conductor. We believe that this high charge requirement is the reason for the failure of $C_{12}AsF_6$ to pick up excess fluorine. As may be seen from Table 4, all of the fluorinated $C_xAsF_6{\cdot}yF_2$ materials that have been studied are poor conductors. If the vacancies of the $C_{12n}AsF_6$ anion array are occupied by F^{-} ions as proposed, the periodic anion array is not much denser than in either $C_{12}^{+}AsF_6^{-}$ or $C_{8\underline{n}}AsF_5$. This increase in charge may well be the decisive factor in bringing about the lower conductivity.

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Table 1. Composition, thickness, oscillator voltage, and electrical conductivity of the HOPG-AsF_5 compounds C_xAsF_5.

Sample	Gravimetric Composition, x	t/t_o[a]	V/V_o[b]	σ/σ_G[c]
1	16	1.71	20.8	12.2
	7.9	2.45	29.6	12.1
2	16	1.72	20.0	11.6
	12.7	1.96	22.1	11.3
3	8.3	2.8	30.0	12.4[d]
4	9.4	2.32	25.3	10.9
5	16.0	1.76	22.3	12.7
6	16.4	1.82	22.1	12.1
7	18.6	1.68	17.1	10.2
8	20	1.65	16.7	10.1
9	22.9	1.53	18.3	12.0
10	24.8	1.48	18.3	12.4
11	34	1.39	16.9	12.2
12	35.9	1.38	13.0	9.4
13	39.7	1.35	15.9	11.8

[a] Systematically 5% too large, perhaps because of microscopic cracking. There is also a 3 - 5% measurement uncertainty.

[b] The voltage measurements have a 5% estimated uncertainty.

[c] $\sigma/\sigma_G = (V/V_o) \times (t/t_o)^{-1}$ has an estimated 10% uncertainty.

[d] Calculated using the theoretical $t/t_o = 2.42$.

Table 2. The effect on composition, thickness, and conductivity of alternately pumping and adding AsF_3 to four different HOPG-AsF_5 samples.

Sample	Measured Parameters	A	Pump → B	Add AsF_3 → A'	Pump → B'	Add AsF_3 → A"	Pump → B"
1	Gravimetric composition	$C_{16.0}AsF_5$	$C_{23.9}AsF_6$	$C_{18.1}AsF_5$			
	t/t_o	1.76	1.67	1.71			
	σ/σ_G	12.7	11.4	11.5			
2	Gravimetric composition	$C_{22.9}AsF_5$	$C_{30.7}AsF_6$	$C_{24.4}AsF_5$	$C_{39.2}AsF_6$	$C_{26.4}AsF_5$	$C_{38.3}AsF_6$
	t/t_o	1.53	1.49	1.51	1.44	1.48	1.39
	σ/σ_G	12.0	12.6	12.4	12.4	11.3	11.2
3	Gravimetric composition	$C_{24.8}AsF_5$	$C_{32.3}AsF_6$	$C_{25.4}AsF_5$	$C_{37.2}AsF_6$	$C_{25.0}AsF_5$	$C_{33.7}AsF_6$
	t/t_o	1.48	1.46	1.48	1.43	1.48	1.43
	σ/σ_G	12.4	12.0	12.1	12.0	11.0	11.3
4	Gravimetric composition	$C_{16.4}AsF_5$	$C_{22.6}AsF_6$				
	t/t_o	1.82	1.68				
	σ/σ_G	12.2	12.7				

Table 3. Composition, relative thickness, and relative conductivity of $HOPG^+-AsF_6^-$ salts prepared from $O_2^+AsF_6^-$.

Sample	Gravimetric Composition	t/t_o	σ/σ_G
HA 11	$C_{14.6}AsF_6$	2.24	4-6
HA 3	$C_{30.9}AsF_6$	1.59	11.1

Table 4. The effect on composition, thickness, and conductivity of adding F_2 to HOPG-AsF_5 compounds.

	Before adding F_2			After adding F_2		
Sample	Gravimetry	t/t_o	σ/σ_G	Gravimetry	t/t_o	σ/σ_G
3	$C_{8.3}AsF_5$	2.8	12.4[a]	-[b]	-[b]	11.6[a]
2	$C_{12.7}AsF_5$	1.96	11.3	$C_{12.7}(AsF_6)_{0.66}(AsF_5)_{0.34}$	-	0.53
7	$C_{18.6}AsF_5$	1.68	10.2	$C_{18.6}AsF_6\cdot 0.19F_2$	2.27	2.7
8	$C_{20}AsF_5$	1.65	10.1	$C_{11}AsF_6$[c]	2.34	2.17
				$C_{7.8}AsF_6$[c]	-	1.54[a]
13	$C_{39.7}AsF_5$	1.35	11.8	$C_{39.7}AsF_6\cdot 0.5F_2$	1.62	8.1

[a] Calculated using the theoretical $t/t_o = 2.42$.

[b] Gravimetry and thickness measurements were not made until after removing AsF_5. See text.

[c] AsF_5 also added to consume excess F_2.

Table 5. Effect of titrating an HOPG-AsF_6 sample with AsF_3.

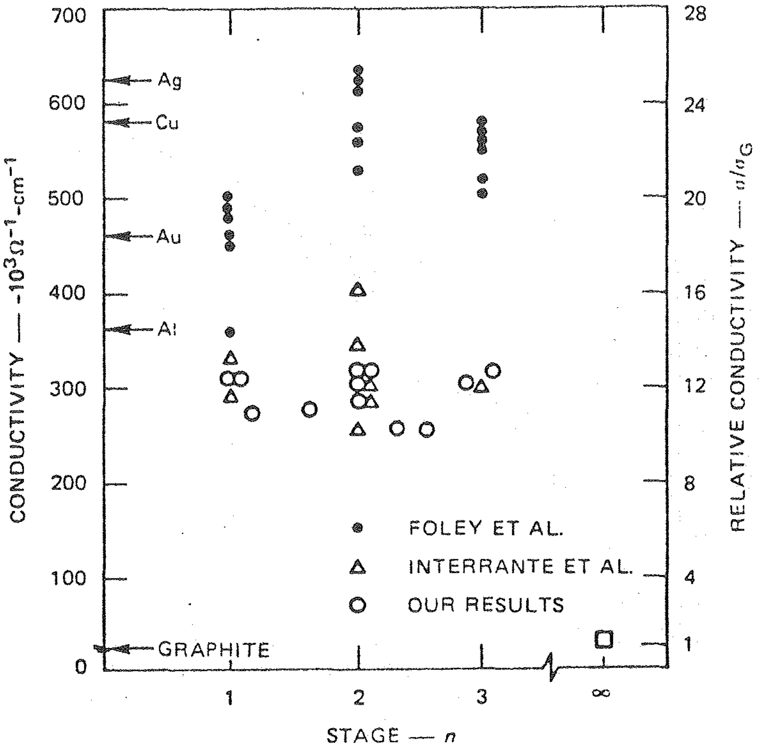
Sample Parameter	$C_{39.7}AsF_6 \cdot (F_2)_{0.5}$	$+ AsF_3 \longrightarrow$	$C_{19.5}AsF_5$
$\underline{m}$ (mg)	25.0	5.0	30.0
$\underline{t}/\underline{t}_o$	1.62		1.68
V/V_o	13.2		17.4
σ/σ_G	8.1		10.4

Figure Captions

Fig. 1 The conductivities of the HOPG-AsF_5 compounds $C_{8n}AsF_5$, where n is the stage, as determined by three different groups of researchers.

Fig. 2 Relative conductance of the carbon planes as a function of stage for three different samples. The open circles are from Interrante *et al*. [4] and the solid points correspond to two of our samples. The straight line between the n= 10 and n = 2 points is a least-square fit to that data.

Fig. 3 Schematic representation of a stage-n graphite compound. In a simplified scheme we consider the electrical conductance (per repeat distance) to result from the sum of contributions from the $2m$ layers with conductivity σ_h and from the $n - 2m$ layers with conductivity σ_ℓ.



700
600
500
400
300
200
100
0
Ag
Cu
Au
Al
GRAPHITE
28
24
20
16
12
8
4
1
CONDUCTIVITY — $10^3 \Omega^{-1}$-cm^{-1}
RELATIVE CONDUCTIVITY — σ/σ_G
FOLEY ET AL.
INTERRANTE ET AL.
OUR RESULTS
1
2
3
∞
STAGE — n

Figure 1

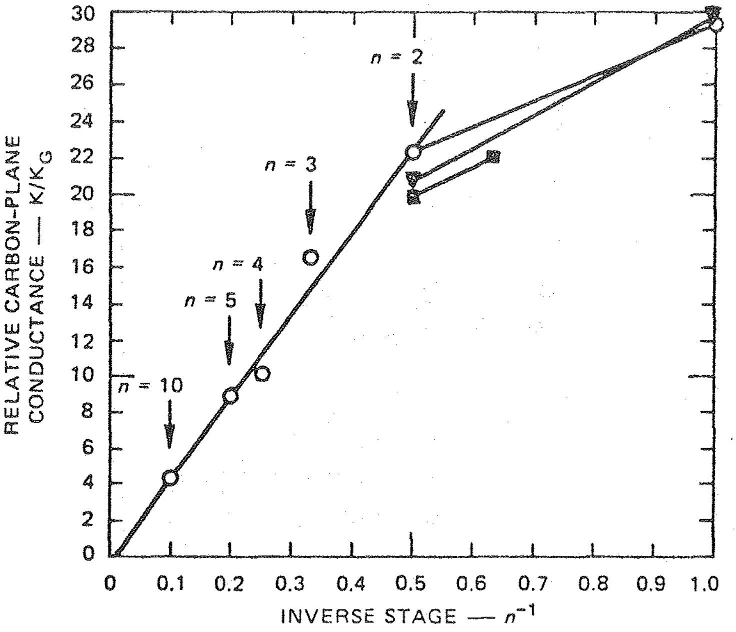
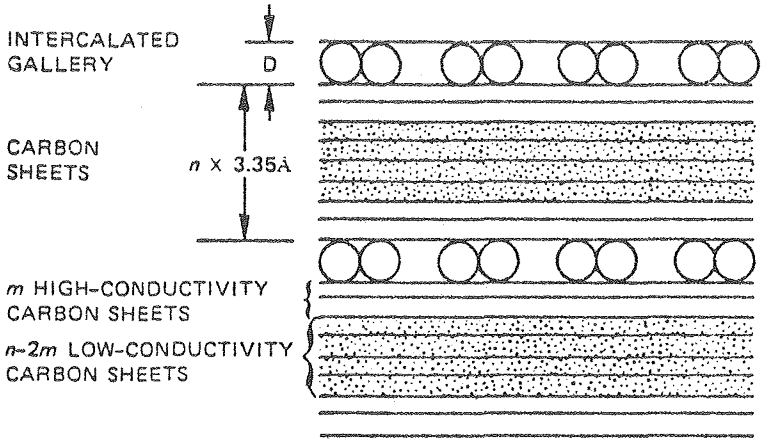

RELATIVE CARBON-PLANE CONDUCTANCE — K/K_G
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
INVERSE STAGE — n^{-1}
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
$n = 10$
$n = 5$
$n = 4$
$n = 3$
$n = 2$

FIGURE 2



INTERCALATED GALLERY
D
CARBON SHEETS
$n \times 3.35$Å
m HIGH-CONDUCTIVITY CARBON SHEETS
n–2m LOW-CONDUCTIVITY CARBON SHEETS

FIGURE 3