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Direct Synthesis of Stage 1–3 Intercalation Compounds of Arsenic Pentafluoride in Graphite

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Uniform stage 1–3 AsF_5–graphite intercalation compounds were prepared by direct interaction of AsF_5 vapor with highly oriented pyrolytic graphite under isothermal conditions. The compounds were characterized using x-ray and gravimetric analyses coupled with observation of the *c*-axis thickness increase. The *c*-axis repeat distance, I_c, followed the relation $I_c = (4.75 + n3.35)$ Å, where n = stage. The stoichiometry of stages 1–3 corresponded to $C_{8n}AsF_5$. The *c*-axis thickness increase proved to be a reliable indicator of stage for stages 1–3; however, more dilute materials were invariably inhomogeneous.

Intercalation is the process of inserting foreign atoms or molecules between the layers of a lamellar host material. Although intercalation of graphite has been known for over 40 years and many types of atoms and molecules have been intercalated,[1,2] no definitive explanation exists for the chemical bonding involved.

Currently, there are two major interests in graphite intercalation compounds. First, in the intercalation process the reactivity of the intercalant is severely modified,[3] hence potential use in selective catalysis can be envisioned. Second, intercalation compounds are synthetic metals.[1,2] They display properties typical of metals, especially high infrared reflectance and high electrical conductivity.

As part of a broad-based investigation into the solid-state properties of graphite intercalation compounds, we have synthesized the first uniform-stage compounds of highly oriented pyrolytic graphite (HOPG) and AsF_5. The stoichiometry of these compounds was observed to be $C_{8n}AsF_5$, where n = stage. (Stage is the number of contiguous carbon layers between successive intercalant layers). Earlier investigators utilizing grafoil and powdered graphite reported the formation of an ASF_5 graphite compound of stoichiometry $C_{10}AsF_5$.[4] However, while their published x-ray data indicated that intercalation had occurred, it did not indicate the formation of a unique stage material.

Recent measurements on uniform AsF_5–graphite compounds have shown that the basal-plane (*a* axis) electrical conductivity can be as high as that of silver,[5] the best elemental conductor. Since the envionmental stability of the higher stage compounds is promising,[6] AsF_5–graphite is a potentially practical synthetic metal. The synthesis of these compounds is the subject of this paper.

Experimental Section

The material used throughout this work was highly oriented pyrolytic graphite (HOPG) which was obtained from Union Carbide and used without further purification. The spread of the *c* axes in this polycrystalline material is of the order of 1° and the crystallite sizes are of the order of a few microns. Most of the graphite samples to be intercalated were cut to 5 × 8 mm^2 *c*-face rectangles using a 0.025-cm diamond string saw. Additional samples from 5 × 5 mm^2 to 6 × 20 mm^2 were also intercalated; many of these were cut to size using air abrasion instead of the string saw. The initial thickness of most samples was in the range 0.025–0.064 cm; these *c*-axis thickness measurements were made using a microscope with a calibrated reticule (sensitivity = 5×10^{-4} cm). The initial weight of the samples fell in the range 15–50 mg (±0.05 mg).

The arsenic pentafluoride (Ozark Mahoning) was checked for purity by vapor-phase molecular weight determinations. In most instances it was found acceptable as received (±1% of theoretical value 169.9); when unacceptable it was purified by trap-to-trap distillation and rechecked.

All volatile materials were manipulated utilizing standard high-vacuum techniques in a glass system equipped with glass–Teflon valves. All intercalated materials were handled under a dry nitrogen atmosphere since the lowest stage compounds exhibited extreme sensitivity to moisture.

All AsF_5–graphite intercalation compounds were prepared in an inverted h-shaped Pyrex reactor equipped with a glass–Teflon valve on the side arm. The main reactor tube was made of 0.5-in. o.d. glass, the top of which was fitted with a Swagelok ss plug fitted with Teflon ferrules. This arrangement allowed easy insertion of the solid graphite reactant and removal of the intercalated product from an otherwise closed system. The typical total volume of these reaction vessels was 10 mL. Reactions containing up to 3.6 atm of AsF_5 were successfully executed without leakage through the Swagelok connection. The sample of graphite to be intercalated was supported in the reactor in a loose Pt wire spiral which performed two functions. First, it held the graphite in a stable position such that consistent thickness measurements could be made in situ. Second, it suspended the graphite above the bottom of the reactor. This second function enabled the intercalation process to proceed entirely in the vapor phase without contact with AsF_5 liquid during the initial warming process.

In a typical reaction a known amount of AsF_5 (0.5–1.5 ± 0.03 mmol) was condensed at −196 °C into the bottom of the reaction vessel containing the suspended graphite. Since only the bottom of the vessel was cooled the graphite did not vary appreciably from room temperature. The reaction was started by allowing the AsF_5 to warm to 23 °C, at which temperature it is all in the vapor state. The initial warming period mentioned above, during which the AsF_5 warms from −196 to +23 °C, was typically less than 2 min. No observable reaction (thickness) occurred during this time. For a typical 35-mg sample and initial pressure of 1 atm, the final pressure was 0.5 atm over a

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second stage compound. During the intercalations the *c*-axis thickness was monitored at frequent intervals.

As indicated in the Results and Discussion section, relative *c*-axis thickness increase, $\Delta t/t_0$ (t_0 = initial thickness), proved to be a reliable indication of the stage of intercalation for stages 1–3. It was the primary monitor used to decide when to terminate reactions at a specific stage of intercalation. Unfortunately, utilization of this technique in attempts to prepare fourth and higher stage compounds resulted in materials of mixed stages (x ray, gravimetric analysis).

Reactions were stopped by opening the vessels in a nitrogen atmosphere and removing the intercalated graphite from the system. This method was utilized as opposed to ambient temperature vacuum removal of the excess AsF_5 because the intercalated samples of lower stage tended to severely exfoliate (essentially explode physically) under vacuum.

Reaction times needed to produce uniform stages 1, 2, and 3 were on the order of 20–73 h for stage 1, 5–20 h for stage 2, and 2–5 h for stage 3. Precise reaction times for a given sample size and initial pressure cannot be quoted because the reaction rates were strongly sample dependent. There was a general trend toward faster reactions as the initial AsF_5 pressure was increased (range 1.0–3.6 atm); however, the scattering was so large as to preclude a determination of the pressure dependence of the reaction rate. Stage 1 compounds would not form in reasonable times (days) when the initial AsF_5 pressure was less than 1.0 atm. This is not an indication of a true pressure–composition effect, however, because stage 1 was eventually achieved with extended reaction times (weeks).

Gravimetric and x-ray analyses, coupled with the *c*-axis thickness measurements, were used to characterize the resulting compounds. Gravimetric analyses were made by weighing the intercalated samples while enclosed in preweighed Teflon containers. X-ray data were obtained on a Bragg diffractometer with a Cu source. The moisture sensitivity of the intercalated materials necessitated the construction of a special x-ray holder, which consisted of an aluminum body with "plastic wrap"[7] window and a Kel-F screw plug. Samples were transferred under dry nitrogen from the Teflon container into this holder; the *c* face of the sample was placed against the window. The Kel-F screw plug was adjusted to support the sample against the window; Teflon tape on the screw threads ensured a closed system. The orientation of the holder was such that only (00*l*) reflections were observed.

Results and Discussion

Accurate characterization of the intercalation compounds received a high priority in this work because uniformity of stage was crucial to analysis of the various conductivity, reflectance, resonance, and diffraction measurements performed on these materials. Characterization was based on x-ray data, observed *c*-axis thickness increase, and gravimetric analysis; homogeneity of an intercalated compound was indicated by the agreement of all three techniques. In contrast, x-ray data for inhomogeneous samples indicated a mixture of stages, and the weight uptake did not agree with that expected from the observed thickness increase.

The x-ray analysis directly indicated both the existence of a lamellar compound and its stage. The (00*l*) reflections from the samples were analyzed using Bragg's equation. The reflection peaks were sharp (<0.3°) and fell into a clearly defined pattern with each peak corresponding to a definite order of reflection. Linear least-squares fits were made to plots of the inverse of the d spacings vs. the reflection order, *l*. The *c*-axis repeat distances, I_c, were determined from the optimized slopes of these plots.

The observed repeat distances, I_c, as well as the calculated x-ray penetration depths for stages 1–5 are shown in Table I. In graphite the spacing between adjacent planes is 3.35 Å, thus analysis of these data yields the relationship

$$I_c = 4.75\ \text{Å} + n(3.35)\ \text{Å} \qquad (1)$$

where *n* is the stage of the compound. The lattice expansion (4.75 Å) is consistent with the size of an AsF_5 molecule calculated from covalent radii.

Table I. Observed *c*-Axis Repeat Distances, I_c, Theoretical and Experimental Thickness Expansion Ratios ($\Delta t/t_0$) for AsF_5-Graphite, and Theoretical X-Ray Penetration Depths, *d*[a]

Stage	I_c, Å	$\Delta t/t_0$ (theory)	$\Delta t/t_0$ (exptl)	*d*, cm
1	8.10 ± 0.02	1.42	1.41 ± 0.02	0.014
2	11.40 ± 0.02	0.70	0.71 ± 0.02	0.018
3	14.81 ± 0.04	0.47	0.47 ± 0.02	0.022
4	18.31 ± 0.04	0.35		0.026
5	21.51 ± 0.04	0.28		0.030

[a] Calculated from μ_i/ρ_i ratios taken from J. A. Ibers and W. C. Hamilton, Ed., "International Tables for X-Ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England.

Table I also presents theoretical and experimental values of the *c*-axis thickness increase, $\Delta t/t_0$. The theoretical values are derived from the x-ray data. Experimental values for fourth and fifth stage are not listed because it was not possible to prepare homogeneous compounds of those stages. The excellent agreement obtained from stages 1–3 is clearly evident, however.

As discussed below, gravimetric analysis of the stage 1–3 compounds consistently indicated a stoichiometry of $C_{8n}AsF_5$, where *n* = stage. This is in contrast to a previous report of $C_{10}AsF_5$ for first stage material from powder or grafoil.[4] First stage (C_8AsF_5) compounds were observed to decompose regardless of sample size to compositions of approximately $C_{10}AsF_5$ when they were left exposed for several hours in a large (~10 L) volume of dry N_2. When x rayed after exposure they were found to be a mixture of stage 1 and 2.

The physical properties of AsF_5–graphite vary markedly with stage. While the *c* faces remain specular upon intercalation, the color ranges from metallic blue for stage 1 to metallic silver for stage 3. The optical reflectance is high and possesses a metallic behavior,[8] but this varies as a function of stage. The electrical conductivity rivals the best metals;[5] it is the highest for stage 2. The environmental stability generally decreases with increasing AsF_5 composition. The lowest stages emit fumes of white solids when exposed to moist air, while samples of mixed higher stages displayed an insignificantly small weight loss even when exposed to air for a period of days.

These intercalation compounds are stable sealed in small (<1 mL) Pyrex ampoules under dry nitrogen but decompose under dynamic vacuum. The stage 1 compound actually explodes when instantly exposed to vacuum at ambient temperatures, indicating a fast initial rate of deintercalation under these conditions. Under static vacuum in a 10-mL vessel one sample (46.5 mg, 5.5 × 8 mm) went from C_9AsF_5 to $C_{11.4}AsF_5$ in 5 h. An additional hour under dynamic vacuum produced $C_{14.3}AsF_5$ and 16 h, $C_{26}AsF_5$. The weight lost by the sample (direct weighing) corresponded to the number of moles of deintercalated material (*PVT* measurement) if that material was assumed to be AsF_5. This is significant as it implies that AsF_5 is not altered in the intercalation process.

Two factors make preparation of uniform stage 1–3 AsF_5–graphite intercalation compounds practical by the direct vapor-phase method described herein. First, as shown in Figure 1, there is an obvious, spontaneous "staging" observed as plateaus in the *c*-axis thickness plotted as a function of reaction time. These plateaus occur at expansions corresponding to specific stages calculated from x-ray data repeat distances; see Table I. Second, there is excellent correlation between the visually observed *c*-axis thickness increase and the actual stage of intercalation. There is no fraying of the sample's edges or "exfoliation". This characteristic allows accurate tracking of the thickness increase with simple optical equipment.

Early in the reaction a series of annular steps appears on the *c* face of the sample. These steps continually propagate

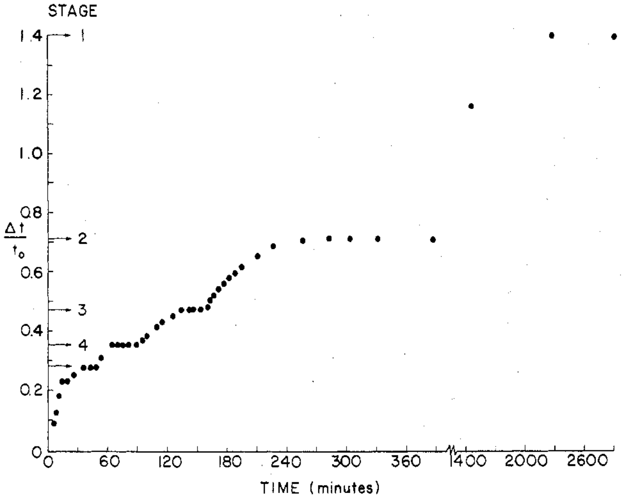

Figure 1. Plot of c-axis expansion ratio, $\Delta t/t_0$, vs. reaction time for a typical intercalation of arsenic pentafluoride into graphite.

toward the center of the sample; by the time the compound has reached third stage the steps have disappeared. Further c-axis expansion of the compound occurs uniformly, making the thickness measurements an accurate reflection of the stage for stages 3–1.

The presence of the steps explains both the "fourth" and "fifth" stage plateaus in Figure 1 and the inability to produce homogeneous compounds of these stages in an isothermal system. Thickness measurements are made at the sample's edge; the steps arise from the diffusion of the intercalant between carbon layers toward the center of the sample. Thus when the edge is fourth or fifth stage the center is more dilute, conversely by the time the center has reached fourth stage the edge is third. The reason for the uniform expansion beyond third stage is unknown.

The correlation of thickness increase to stage and stoichiometry is shown in Figure 2. This is a plot of 100/% AsF_5 intercalated vs. $t_0/\Delta t$. The circles are the theoretical values for n = 1–4 based on $C_{8n}AsF_5$ and a c-axis thickness change calculated from repeat distances (x ray). The other data are from a number of independent reactions in which experimental thickness change, gravimetric results, and x-ray data were obtained. The excellent agreement demonstrated in Figure 2 between experimental and theoretical values reflects the predictable character of the reaction; this was further confirmed by the uniformity of stage 1–3 samples indicated by x-ray analysis. In contrast, the values of 100/% AsF_5 obtained from attempted stage 4 preparations are scattered, as expected from the previous discussion and the experimentally observed mixed-stage x-ray data obtained on these samples.

The spontaneous staging observed in these AsF_5 intercalations is an unusual phenomenon. While it has been known for some time that a two-temperature system can be used to vary the stage of an intercalation compound by varying the temperature differential, we believe the AsF_5 system is the first to exhibit spontaneous successive steps in c-axis thickness under isothermal conditions which accurately reflect the stage of the compound. All of the reactions observed exhibited this staging; however, the location and duration of the plateaus in terms of reaction time varied somewhat from sample to sample. A comparison of AsF_5–graphite with the other group 5 pentafluoride, SbF_5, known to intercalate in graphite is instructive. AsF_5 requires both milder reaction conditions (temperature) and shorter reaction times to reach the same stage of intercalation.[9] The stability of the resultant AsF_5 compounds under dynamic vacuum is lower than their SbF_5 counterparts. Despite the fact that the intercalation process is much faster with AsF_5, physical distortion other than the expected c-axis expansion of the graphite is not observed, unlike the visually apparent edge fraying in SbF_5 intercalations. AsF_5 intercalation reactions are much easier to terminate at a desired stage due both to more accurate c-axis thickness measurements (no edge fraying) and to definitive "staging"; this behavior leads to more uniform materials. Finally, as expected, the c-axis repeat distances for comparable stages are smaller for the AsF_5–graphite by the approximate difference of the covalent diameter of Sb and As ($d_{Sb} - d_{As}$ = 0.40 Å; ΔI_c = 0.36 Å).

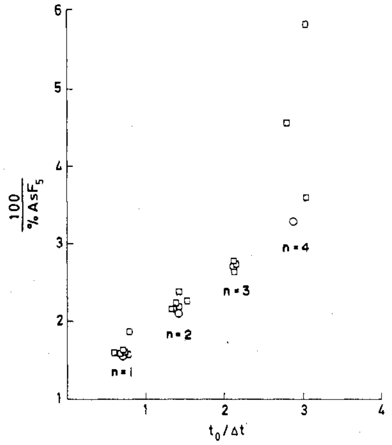

Figure 2. Plot of 100/% AsF_5 intercalated in graphite vs. corresponding ratio of initial c-axis thickness to change in c-axis thickness for several independent reactions. The ○ represent theoretical values for stages 1–4 based on $C_{8n}AsF_5$ stoichiometry and c-axis thickness change calculated from x-ray repeat distance, I_c.

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Registry No. AsF_5, 7784-36-3; graphite, 7782-42-5.

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