Preparation and Properties of New Graphite–Fluorine Intercalation Compounds

I. Palchan,[a,b] D. Davidov,[a] and Henry Selig*[b]

[a] Racah Institute of Physics and [b] Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

Graphite–fluorine intercalation compounds with the general formula C_xF ($x > 2$) have been prepared, having basal plane conductivities comparable to the highest conductivity among known intercalation compounds.

The only chemical compounds between fluorine and graphite have been the poorly conducting compounds CF, C_2F, and C_4F.[1] Recently Mallouk and Bartlett reported graphite fluoride, C_xF ($5 > x > 2$), made by the intercalation of graphite with fluorine in the presence of *liquid anhydrous hydrogen fluoride*.[2] The conductivities of these compounds are still not very high, although they exceed considerably those of the hitherto known covalent graphite fluorides. Our experimental investigations, carried out concurrently, show that C_xF ($x > 2$) can be prepared by exposing HOPG (highly oriented pyrolytic graphite) to neat fluorine gas. In some experiments the fluorine gas had been passed through a freshly regenerated Matheson Co. NaF tower to remove HF. The rate of intercalation is rather slow and strongly depends on the fluorine pressure. The presence of minute amounts of catalysts such as AsF_5, IF_5, or OsF_6, considerably accelerates the reaction.

X-Ray diffraction studies (00*l* diffractograms) indicated the formation of second, third, and fourth stage compounds with *c*-axis repeat distances of $d = 6.0 + (n - 1) \times 3.35$ Å ($n =$ stage). Changes in sample thickness correspond approximately to theoretical expansions calculated from these *X*-ray results.

Basal plane conductivities, σ_a, were measured by the contactless r.f. technique[3] at room temperature. Relative to the basal plane conductivity of HOPG, σ_g, these were $\sigma_a:\sigma_g$ = *ca.* 5—7 for stage II compounds (at least 5 different samples of pure stage II were prepared); $\sigma_a:\sigma_g = $ *ca.* 11 for a mixture of stage III (60%) and stage IV (40%); $\sigma_a:\sigma_g = $ *ca.* 9 for a mixture of stage II (50%) and stage IV (50%); $\sigma_a:\sigma_g = $ *ca.* 8 for a mixture of stage IV (30%) and HOPG (70%); and $\sigma_a:\sigma_g$ = *ca.* 6 for pure stage IV. These conductivities are considerably greater than those reported earlier.[2] This is also consistent with previous reports (on different types of intercalant) that mixed stages show higher conductivities than those of the pure components.[4] The density, ρ, of our graphite intercalation compound (GIC) is significantly reduced with respect to that of pure HOPG (ρ_{HOPG}), *i.e.* $\rho:\rho_{HOPG} = $ *ca.* 0.78 to 0.9. The specific conductivity per unit weight is, thus, larger by a factor of two than that of copper. Weight uptakes indicated chemical compositions of about C_5F (stage II) and $C_{16}F$ (stage IV). This was confirmed by electron microprobe analyses.
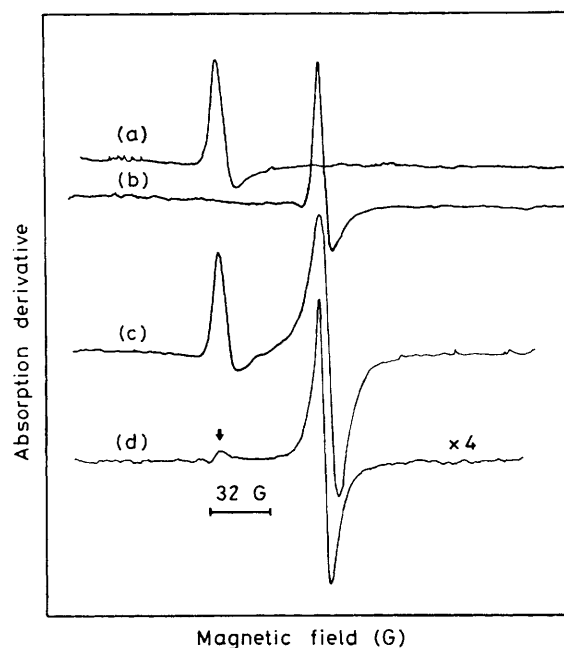
Figure 1. E.s.r. signal (absorption derivative) *vs.* magnetic field ($1 G = 10^{-4}$ T). (a) Pure HOPG, $\vec{H} \parallel$ *c*-axis, $g = $ *ca.* 2.047; (b) pure HOPG, $\vec{H} \perp$ *c*-axis, $g = $ *ca.* 2.002; (c) same as (a), *immediately* after exposure to fluorine (*ca.* 2000 Torr) (note strong signal appearing at $g = $ *ca.* 2.000); (d) same as (c) after 80 min exposure to F_2 [note drastic reduction in intensity of HOPG signal (arrow)]. Signal intensity is 4 times that indicated in (a)—(c).

In situ e.s.r. measurements were carried out at room temperature on a Varian E-line spectrometer. Pure HOPG exhibits a single, strongly anisotropic e.s.r. line,[5] Figures 1(a) and 1(b).

With the magnetic field orientation parallel to the $\vec{c}$-axis, the HOPG sample was exposed to a fluorine pressure of *ca.* 2000 Torr. In addition to the spectrum of 'pure' HOPG, a new and relatively strong e.s.r. line appears *immediately* upon exposure

to fluorine, Figure 1(c). In contrast to the HOPG spectrum, this line exhibits only a slight angular dependence with anisotropy of less than 1 G. Its relatively large intensity indicates significant charge transfer between the fluorine molecules and a nearby surface layer of the HOPG. The latter is indicated by the relatively small A/B ratio (ca. 1) (according to the notation of Feher and Kip)[6] with respect to the e.s.r. signal in HOPG.

Measurements of the e.s.r. signal as a function of time over a period of three days clearly indicate the following features. (a) The signal associated with HOPG disappears with time, Figure 1(d). (b) The signal intensity of the e.s.r. line associated with fluorine increases. (c) The A/B ratio increases significantly from ca. 1 to ca. 8 over a period of three days. (d) The e.s.r. line widths narrow with time and become $\Delta H = $ ca. 0.6 G. This line width is of the same order as that of stage II $C-AsF_5$ and $C-PF_5-F_2$.[5] These features can be explained by a time-dependent intercalation process. The A/B ratio measures roughly the ratio of layer thickness, t, to skin depth. The intercalation process is initially merely a surface effect, but becomes a bulk property of the resulting GIC. This means a larger t and consequent increase of the A/B ratio with intercalation. It appears, therefore, that the line width narrowing as a function of time is indicative of the bulk intercalation process.

At present, the identity of the intercalated fluorine species is unknown. If it were only fluoride ion, the filled layer spacing should be 4.7 Å, assuming a close-packing model. The value of 6.0 Å obtained may indicate the presence of mobile molecular fluorine, but the presence of bifluoride ions cannot be excluded.

References

1 P. Kamarchik, Jr., and J. L. Margrave, *Acc. Chem. Res.*, 1978, **11**, 296.
2 T. Mallouk and N. Bartlett, *J. Chem. Soc., Chem. Commun.*, 1983, 103.
3 C. Zeller, A. Denenstein, and G. M. T. Foley, *Rev. Sci. Instrum.*, 1979, **50**, 602.
4 M. J. Moran, J. W. Milliken, C. Zeller, R. A. Grayeski, and J. E. Fischer, *Synth. Met.*, 1981, **3**, 269.
5 O. Milo, I. Palchan, D. Davidov, and H. Selig, presented at the 3rd International Conference on Graphite Intercalation Compounds, Pont-a-Mousson, France, May 23—27, 1983.
6 G. Feher and A. F. Kip, *Phys. Rev.*, 1955, **98**, 337; J. F. Dyson, *ibid.*, p. 349.