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THE ROLE OF FLUORINE CHEMISTRY IN STUDIES OF THE SYNTHETIC METALS: INTERCALATED GRAPHITE AND DOPED POLYACETYLENE

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The degree of charge transfer involved in the intercalation of graphite has been the subject of controversy. Information on this process has been obtained from the intercalation of transition metal hexafluorides MF_6 (M = Mo,Tc,Re,Os,Ir) into highly oriented pyrolytic graphite (HOPG). These hexafluorides are of interest, because they comprise a unique group of intercalants differing mainly in their electronic configurations and oxidizing properties. The intercalation may generally be written as $nC + MF_6 \rightarrow C_n^{+x}(MF_6^-)_x(MF_6)_{1-x}$ where x denotes the degree of charge transfer. In some cases x can be extracted from simultaneous ESR and susceptibility studies of the magnetic intercalate species. For OsF_6 such studies confirm earlier conclusions by Bartlett that $x = 1$.

Similar measurements on graphite compounds with MoF_6 lead to $x \approx 0.2$. For HOPG/ReF_6, susceptibility measurements indicate $x \sim 0.35$. Combining these results with data on TcF_6 and PtF_6 compounds show that the c-axis spacing of an occupied layer is a smooth function of the degree of charge transfer and the electron affinity of the MF_6. Only graphite compounds with IrF_6 deviate from these relations indicating that IrF_6 may have a lower electron affinity than previously estimated and/or that it is partially reduced to IrF_6^{2-} in the process of intercalation, i.e. $x > 1$.

Results of doping polyacetylene with MF_6 parallel those with graphite, causing large increases in conductivity. The maximum conductivities attainable vary inversely with the electron affinity of the MF_6. Here, too, IrF_6 does not fit this generality, which may mean that IrF_6 undergoes a different reaction upon doping than the other MF_6 compounds.